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Molecules without the Born-Oppenheimer approximation

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The University of Arizona, 1992
MOLECULES WITHOUT THE
BORN-OPPENHEIMER APPROXIMATION

by

Pawel M. Kozlowski

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1992
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Pawel M. Kozlowski entitled *Molecules Without the Born-Oppenheimer Approximation*.

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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ABSTRACT

General formalism for the application of explicitly correlated Gaussian-type basis functions for nonadiabatic calculations on many-body systems is presented. In this approach the motions of all particles (electrons and nuclei) are correlated at the same time. The energy associated with the external degrees of freedom, i.e., the motion of the center-of-mass, is eliminated in an effective way from the total energy of the system. Methodology for construction of the many-body nonadiabatic wave function and algorithms for evaluation of the multicenter and multiparticle integrals involving explicitly correlated Gaussian cluster functions are derived and computationally implemented. Then analytical derivation of multi-center and multiparticle integrals for explicitly correlated Cartesian Gaussian-type cluster functions is demonstrated. The evaluation method is based on application of raising operators which transform spherical cluster Gaussian functions into Cartesian Gaussian functions. Next, the Newton-Raphson procedure for optimization of the non-linear parameters (Gaussian exponents) appearing in the Gaussian-type cluster functions is developed. The procedure employs the first and second analytical derivatives of the variational functional with respect to the Gaussian exponents. The computational implementation of Newton-Raphson optimization procedure is described and some numerical calculations are presented. Finally, the methodology for generating higher nonadiabatic rotational states is presented.
CHAPTER I

BORN-OPPENHEIMER APPROXIMATION AND BEYOND

1.1 INTRODUCTION

The majority of chemical systems and chemical processes can be theoretically described within the Born-Oppenheimer (BO) approximation [1,2] which assumes that nuclear and electronic motions can be separated. With this separation, the states of the electrons can be determined from the electronic Schroedinger equation, which depends only parametrically on the nuclear positions through the potential energy operator. As a result, the calculations of dynamical processes in molecules can be divided into two parts; the electronic problem is solved for fixed positions of atomic nuclei giving a potential surface, and then the nuclear dynamics on the calculated electronic potential surface are considered. The most important consequence of the above approximation is the potential-energy surface (PES) concept, which provides a conceptual as well as a computational base for molecular physics and chemistry. Separation of the nuclear and electronic degrees of freedom has had significant impact and has greatly simplified the theoretical view of the properties of molecules. The molecular properties can be rationalized by considering the dynamics on a single electronic PES, in most cases the PES of the ground state. Phenomena and processes such as internal rotational barriers, dissociation, molecular dynamics, molecular scattering, transitions to other electronic states, and infrared and microwave spectroscopy have simple and intuitive interpretations based on the PES concept [3].

Theoretical determination of PES’s for ground and excited states has been one of the primary objectives of quantum chemistry. One of the most significant
developments in this area in the last two decades has been the theory of analytical derivatives [4]. This theory involves calculation of derivatives of the BO potential energy with respect to the nuclear coordinates or magnitude of external fields. Besides the use of analytical derivatives in characterizing the local curvature of PES’s, they are required for calculation of electronic and magnetic properties (energy derivatives with respect to applied external field) as well as in calculations of forces and force constants.

Theoretical justification of the BO approximation is not a trivial matter. One should mention here a study presented by Wooley [5-8] and Wooley and Sutcliffe [6]. They draw attention to the fact that the BO approximation cannot be justified in any simple way in a completely nonclassical theory. This is related to the most essential philosophical concepts of quantum mechanics.

An increasing amount of evidence has been accumulated indicating that a theoretical description of certain chemical and physical phenomena cannot be accomplished by assuming separation of the nuclear and electronic degrees of freedom. There are several cases which are known to violate the BO approximation due to a strong correlation of the motions of all particles involved in the system. For these kinds of systems the BO approximation is usually invalid from the beginning. Examples of such types of behavior of particular interest to molecular physicists can be found in the following systems:

- excited dipole-bound anionic states,
- metastable anionic states of polar molecules,
- single and double Rydberg states,
- muonic molecules,
- electron-positonium systems.

One of the most important problems in modern quantum chemistry is to reach “spectroscopic” accuracy in quantum mechanical calculations, (i.e., error less than an order of one μhartree.) Modern experimental techniques such as gas phase ion beam spectroscopy reach accuracy on the order of 0.001cm⁻¹ [9,10]. Such accuracy is rather difficult to accomplish in quantum mechanical calculations even for such small one-electron systems as $H_2^+$, or $HD^+$. To theoretically reproduce the
experimental results with equal accuracy it is necessary to consider corrections beyond the exact solution of the nonrelativistic Schrödinger equation. Naturally, the desire to computationally reproduce experimental accuracy has generated interest in the nonadiabatic approach to molecules. Most work in this area has been done for three particle systems and the majority of the relevant theory has been developed for such restricted cases.

The conventional nonadiabatic theoretical approach to three particle systems has been based on the separation of the internal and external degrees of freedom, i.e., transformation to the center-of-mass (CM) frame. This has been achieved by coordinate transformation. The choice of the coordinate system is not unique and a number of possibilities have been considered by different authors. Some of them will be discussed in more detail in the next section. The coordinate transformation to the CM frame facilitates separation of the Schrödinger equation into a set of uncoupled equations, one representing the translational motion of the CM, and the other representing the internal motion of the system. The next step following coordinate transformation consists of variational solution of the internal eigenvalue problem with a trial function which possesses appropriate rotational properties. "Appropriate" rotational properties include the requirement that the variational wave function be an eigenfunction of the $\hat{J}^2$ operator and its $\hat{J}_z$ component for the whole system defined with respect to CM. Some attempts have been made to solve the nonadiabatic problem for an arbitrary system following the strategy outlined above, however practical realizations have been so far restricted to the three body problem.

A slightly different approach has been taken for diatomic molecules. The derivation of the nonadiabatic equations for diatomic molecules involves two steps. The first step is exactly the same as for three particle systems. The second step is the separation of the rotational coordinates. This separation is accomplished by transforming from the space-fixed axes to a set of rotating molecule-fixed axes. The internal molecular Hamiltonian, which results after removal of the translational and rotational coordinates, contains a number of cross-terms, such as mass polarization terms and terms coupling different rotation eigenfunctions. The cross-terms which
appear in the internal Hamiltonian couple the momenta of the particles which leads to a certain type of correlation of their internal motions. These terms are also responsible for the fact that the total linear momentum and the total angular momentum of the molecule remains constant. In practice further simplifications are made and some coupling terms are neglected in the internal Hamiltonian.

Taking into account the complications resulting from the transformation of the coordinate system we have recently been advancing an alternate approach where the separation of the CM motion was achieved not through transformation of the coordinate system, but in an effective way by introducing an additional term into the variational functional representing the kinetic energy of the CM motion. Our preliminary nonadiabatic calculations on some three and four particle systems have shown that with this new method a similar level of accuracy could be reached as in the standard methods based on explicit separation of the CM coordinates from the internal coordinates. The advantage of the new method is that one can easily extend this approach to systems with more particles due to the use of the conventional Cartesian coordinate system and explicitly correlated Gaussian functions in constructing the many-body nonadiabatic wave function.

1.2 BORN-OPPENHEIMER APPROXIMATION AND ITS VALIDITY

The Born-Oppenheimer (BO) approximation formulated in 1927 [1] and a modification, the adiabatic approximation formulated in 1954 [2], also known as the Born-Huang (BH) expansion, constitute two of the most fundamental notions in the development of the theory of molecular structure and solid state physics. The approximations assume separation of nuclear and electronic motions. The BO approximation and adiabatic approximation have been studied both analytically and numerically. The literature concerning this subject is rather extensive, but some relevant review articles exist, for example by Ballhausen and Hansen [11], Köppel, Domcke and Cederbaum [12] as well as Kresin and Lester [13].
Before we proceed to nonadiabatic theory, for clarity of the presentation let us first summarize some results concerning the BO approximation. This approximation can be theoretically derived with the use of perturbation theory where the perturbation is the kinetic energy operator for the nuclear motion. It is commonly accepted that the BO approximation should be based on the fact that the mass of the electron is small in comparison to the mass of the nuclei. In the perturbation approach to the BO separation of the electronic and nuclear motion, the perturbation parameter is assumed to be $\kappa = (\frac{m_e}{M})^{\frac{1}{3}}$ [1,13,15], where $M$ is the mass of largest nuclei. The total Hamiltonian separates as

$$\hat{H} = \hat{H}_0 + \kappa^{\frac{1}{3}} \hat{T}_N. \quad (1.1)$$

The choice of the perturbation parameter is not unique, since only the magnitude of $\kappa$ is taken into consideration in this expansion rather than its accurate value. This parameter can be also taken as the ratio $\kappa = (\frac{m_e}{\mu})^{\frac{1}{3}}$, where $\mu$ denotes the reduced mass of the nuclei [36].

A different derivation of the BO separation of electronic and nuclear motion was presented by Essen [14]. The main idea of Essen’s work was to introduce coordinates of collective and individual motions instead of nuclear and electronic coordinates. He demonstrated that the size of $m_e/M$ is irrelevant, and that the nature of the Coulomb interactions between particles involved in a system rather than their relative masses is responsible for the separation. Practical realization of some aspects presented in Essen’s paper was proposed by Monkhorst [15] in conjunction with the coupled-cluster method. Monkhorst reexamined the BO approximation and the BH expansion with explicit separation of the CM, which was omitted in the original paper of Born and Oppenheimer. The study of the BO approximation for $(m/M)^{\frac{1}{3}} \to 0$ has been carried out by Grelland [16]. In another recent study Witkowski [17] demonstrated that a more appropriate separation parameter should be the difference in energy levels rather than the mass ratio.

The simplest way of deriving the BO approximation results from the BH expansion, called also the adiabatic approximation. In the adiabatic approximation
[2] the total Hamiltonian,
\[ \hat{H} = \hat{H}_0 + \hat{T}_N, \]  
(1.2)
is separated into the Hamiltonian for the clamped nuclei approximation, \( \hat{H}_0 \), and the kinetic energy operator for the nuclei, \( \hat{T}_N \). The solution for the electronic problem,
\[ \hat{H}_0 \psi_n(r; R) = \epsilon_n(R) \psi_n(r; R), \]  
(1.3)
only parametrically dependent on the nuclear positions, is assumed to be known. In the above equation \( r \) and \( R \) denote the sets of the electronic and nuclear coordinates respectively. The eigenvalue problem with the Hamiltonian of Eq.(1.2)
\[ (\hat{T}_N + \hat{H}_0)\Psi(r, R) = E \Psi(r, R), \]  
(1.4)
can be obtained in terms of the following BH expansion
\[ \Psi(r, R) = \sum_n \chi_n(R) \psi_n(r; R), \]  
(1.5)
which leads to the following set of equations
\[ [\hat{T}_N + \epsilon_n(R) - E] \chi_n(R) = \sum_m \hat{\Lambda}_{nm} \chi_m(R). \]  
(1.6)
The nonadiabatic operator \( \hat{\Lambda}_{nm} \) is given by
\[ \hat{\Lambda}_{nm} = -\int dr \psi_n^* [\hat{T}_N, \psi_m], \]  
(1.7)
where \([\hat{T}_N, \psi_m]\) denotes the commutator. An approximation of equation (1.6) can be created by neglecting the nonadiabatic operators on the right hand side. This leads to the result
\[ [\hat{T}_N + \epsilon_n(R) - E] \chi_n(R) = 0 \]  
(1.8)
which constitutes the BO approximation.

The nonadiabatic coupling operator has the following interpretation: the diagonal part represents the correction to the potential energy resulting from the coupling between the electronic and nuclear motions within the same electronic state,
the off-diagonal part represents the same effect but occurring with a transition to different electronic states. It is well known that neglecting such terms can be invalid for some cases. One of such cases occurs when electronic and vibrational levels are close together or cross each other. This may lead to behavior known as the Jahn-Teller, Renner or Hertzberg-Teller effects and is commonly called multistate vibronic coupling [12]. In order to theoretically describe a system which exhibits this effect, one usually expands the wave function as a product of the electronic and nuclear wave functions, and then solves the vibronic equation. Usually, only a few states need to be taken into consideration in this approach. After reviewing the BO and BH approximations, one can conclude that BH expansion is more useful in practical realizations since the coupling matrix elements can be calculated numerically for particular cases and the nonadiabatic contributions can be accounted for.

Much more difficult from the theoretical point of view are cases when the Born-Oppenheimer approximation is invalid from the beginning, i.e., when the coupling matrix elements $\Lambda_{nm}(R)$ are large for more extended ranges of the nuclear separation. Such types of behavior can be found, for example, for some exotic systems containing mesons or other light particles and in certain nonrigid molecules such as $H^+_s$. In such cases a BH expansion slowly converges, or even diverges. The variational rather than perturbational approach is more appropriate for such cases. The application of the nonadiabatic variational approach leads to a wave function where all particles involved in the system are treated equivalently and are delocalized in the space. Correlation of the motions of particles is most effectively achieved by including explicitly the interparticle distances in the variational wave function.

1.3 NONADIABATIC APPROACHES TO MOLECULES

In the next few subsections we review the nonadiabatic approaches made for (A) three particle systems and (B) diatomic molecules, and in the final subsection (C) we emphasize attempts taken towards theoretical characterization of systems with more than three particles.
1.3.1 Three Particle Systems

The system of three particles with masses \((M_1, M_2, M_3)\) and the charges \((Q_1, Q_2, Q_3)\) with Coulombic interactions between particles is described by the following nonrelativistic Hamiltonian

\[
H_{TOT} = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{P_3^2}{2M_3} + \frac{Q_1 Q_2}{r_{12}} + \frac{Q_1 Q_3}{r_{13}} + \frac{Q_2 Q_3}{r_{23}}. \tag{1.9}
\]

In the above formula for the total Hamiltonian, \(r_i\) and \(P_i\) denote the position and momentum vectors of the \(i\)-th particle respectively, and \(r_{ij} = |r_i - r_j|\). To separate internal motion from external motion, the following transformations are used [19,20,22,25].

\[
R_{CM} = \frac{1}{m_0} (M_1 r_1 + M_2 r_2 + M_3 r_3); \tag{1.10}
\]

\[
p_0 = P_1 + P_2 + P_3; \quad m_0 = M_1 + M_2 + M_3, \tag{1.11}
\]

\[
\rho_1 = r_2 - r_1, \quad p_1 = P_2 - \frac{M_2}{m_0} p_0, \quad \mu_1 = \frac{M_1 M_2}{M_1 + M_2}, \tag{1.12}
\]

\[
\rho_2 = r_3 - r_1, \quad p_2 = P_3 - \frac{M_3}{m_0} p_0, \quad \mu_2 = \frac{M_1 M_3}{M_1 + M_3}. \tag{1.13}
\]

After such transformations the Hamiltonian becomes \(H_{TOT} = T_{CM} + H_{Int}\), where

\[
T_{CM} = \frac{P_0^2}{2m_0} \tag{1.14}
\]

represents the translational energy of the whole system, and

\[
H_{Int} = \frac{p_1^2}{2\mu_1} + \frac{p_2^2}{2\mu_2} + \frac{p_1 \cdot p_2}{M_1} + \frac{Q_1 Q_2}{|\rho_1|} + \frac{Q_1 Q_3}{|\rho_2|} + \frac{Q_2 Q_3}{|\rho_2 - \rho_1|}. \tag{1.15}
\]

The eigenfunctions of \(T_{CM}\) are the plane waves \(\exp(ik_0 \cdot r_0)\) with corresponding eigenvalues of \(k_0/2m_0\).

By solving the eigenvalue problem \(H_{Int} \Psi_{Int} = E_{Int} \Psi_{Int}\), one can determine the internal states of the system. Such classical systems as \(H^-\) [27,32], electron-positron system \(Ps^- (e^- e^+ e^-)\) [18,22,24,33], muonic molecules [18,19,28,29,31-33], and the \(H_2^+\) molecule and its isotopes [19,21,26] were studied with this approach. The internal Hamiltonian represents the total energy of two ficticious particles with
masses \( \mu_1 \) and \( \mu_2 \) which move in the Coulomb potential of a particle with charge \( Q_1 \) located at the origin of the coordinate system. The cross term \( p_1 \cdot p_2/M_1 \), which is proportional to \( \nabla_i \cdot \nabla_j \), represents so called "mass polarization" which results from the nonorthogonality of the new coordinates. Instead of the nonorthogonal transformation one can use an orthogonal one \[36\] which, however, leads to a more complicated expression for the interaction part of the Hamiltonian. It should be mentioned that the choice of the coordinates given by Eqs.(1.12) and (1.13) is not unique. Many different coordinates have been proposed to treat the three particle problem. The most popular coordinates used for such calculations have been the Jacobi and mass-scaled Jacobi coordinates \[29,30,31\], and the hyperspherical coordinates \[23\].

Following Poshusta's \[22\] nomenclature, each stationary state of the total Hamiltonian, \( H_{TOT} \), can be labeled by \( n(k, J, M, \alpha) \) where \( n \) counts the energy levels from the bottom of the \((k, J, M, \alpha)\) symmetry manifold. The above symbols have the following interpretations: translational symmetry preserves conservation of the linear momentum which is indicated by \( k \); rotational symmetry about the CM leads to conservation of the angular momentum which is indicated by \( J \) and \( M \). \( J \) and \( M \) represent the fact that the variational wave function is an eigenfunction of the square of the angular momentum operator and its \( z \)-component); the last term, \( \alpha \), represents the appropriate permutational properties of the wave function.

In the variational approach to solving the internal eigenvalue problem the choice of an appropriate trial wave function represents a difficult problem. One can expect that the most appropriate guess for the internal variational wave function should explicitly depend on interparticle distances since motions of all particles are correlated due to the Coulombic interaction and due to the conservation of the total angular momentum. There are different varieties of such functions. In the majority of three particle applications the Hylleraas functions were used \[18,24,27,28,32,33\]. These functions correctly describe the Coulomb singularities and reproduce the cusp behaviour of the wave function related to particle collisions. Another type of function used in calculations has been Gaussian functions \[22,25,29\] which less properly reflect the nature of the Coulombic singularities but are much easier in computational
implementation. The choice of the variational functions will be discussed in detail in the next Chapter.

Higher rotational nonadiabatic states can be calculated by using variational wave functions with appropriate rotational symmetries corresponding to the irreducible representation of rotation groups in the three dimensional space (this can be accomplished with the use of Wigner rotational matrices). The rotation properties of three particle nonadiabatic wave functions have been recently extensively studied for muonic molecules in conjunction with muon catalyzed fusion [34].

Finally, we would like to mention that the extremely high level of accuracy that has been achieved in the last few years in nonadiabatic calculations as well as in experimental measurements on three particle systems allows testing of the limits of the nonrelativistic quantum mechanical methods [35,43].

1.3.2 Diatomic molecules

The nonadiabatic study for diatomic molecules has been mostly restricted to the $H_2$ molecule and its isotopic counterparts. The nonadiabatic results are well documented in articles presented by Kolos and Wolniewicz [36], Peak and Hirschfelder [41], Kolos [37], and Bishop and Cheng [43]. To demonstrate some theoretical results let us consider the nonrelativistic Hamiltonian for an $N$-electron diatomic molecule in a laboratory-fixed axis,

$$H = -\frac{1}{2M_a} \nabla_a^2 - \frac{1}{2M_b} \nabla_b^2 - \frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + V, \quad (1.16)$$

where $a$ and $b$ represent two nuclei with masses $M_a$ and $M_b$ while $i$ labels the electrons. The vector position of CM is expressed as follows.

$$\mathbf{R}_{CM} = M^{-1}(M_a \mathbf{r}_a + M_b \mathbf{r}_b + \sum_{i=1}^{N} \mathbf{r}_i), \quad (1.17)$$

where

$$M = M_a + M_b + N. \quad (1.18)$$

The separation of the CM motion from the internal motion can be accomplished using one of the following sets of coordinates:
a) Separated-Atom Coordinates [41,37]

\[
R = r_b - r_a, \tag{1.19}
\]

\[
r_{ia} = r_i - r_a, \quad 1 \leq i \leq N_a, \tag{1.20}
\]

\[
r_{jb} = r_j - r_b, \quad N_a + 1 \leq j \leq N, \tag{1.21}
\]

b) Center-of-Mass of Nuclei Relative Coordinates [41,37]

\[
r_{i(ab)} = r_i - (M_a r_a + M_b r_b)(M_a + M_b)^{-1}, \tag{1.22}
\]

(with \(R_{CM}\) defined as previously), and

c) Geometrical Center of Nuclei Coordinates [41,37]

\[
R = r_b - r_a, \tag{1.23}
\]

\[
r_{i\theta} = r_i - \frac{1}{2}(r_a + r_b). \tag{1.24}
\]

The separation of the angular motion of the nuclei can be done by transforming from the space fixed axis system \((X,Y,Z)\) to a set of rotating molecule-fixed axes. The transformation is defined by the two Euler rotations: (i) \(\phi\) about the initial \(Z\) axis and (ii) \(\theta\) about the resultant \(y\) axis

\[
R(\phi, \theta, 0) = \begin{pmatrix}
\cos \theta \cos \phi & \cos \theta \sin \phi & -\cos \theta \\
-\sin \phi & \cos \phi & 0 \\
\sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta
\end{pmatrix}. \tag{1.25}
\]

The coordinates \(R, \theta,\) and \(\phi\) are sufficient to describe the motion of the nuclei. Separation of the CM motion and the rotation leads to a set of coupled equations. The coupling results from the fact that the geometrical center of the molecule and the CM for the nuclei do not coincide exactly with the center for the rotation. Nonadiabatic effects are incorporated by appropriate coupling matrix elements. More detail can be found in papers cited earlier, i.e., [36,37,43] as well as [10,39-42]

We would like to stress that the above approach should only work for systems that do not significantly violate the BO approximation and where the rigid rotor model remains a reasonably good approximation.
1.3.3 Many particle systems

This subsection is devoted to nonadiabatic studies of polyatomic systems. We would like to distinguish two aspects of this problem; the first one is related to the development of theory and the second pertains to practical realizations. The most constructive nonadiabatic view of molecules and critical discussion of the BO approximation has been presented by Essen [14]. The starting point for his consideration was the virial theorem which, following Wooley's earlier study [5], plays an essential role in understanding the nature of molecular systems. Essen demonstrated a quite original view on molecules. This view was later extensively analyzed by Monkhorst [15]. Let us use an excerpt from Monkhorst's paper:

"Invoking only the virial theorem for Coulombic forces and treating all particles on an equal footing, a molecule according to Essen can be viewed as an aggregate of nearly neutral subsystems ("atoms") that interact weakly ("chemical bonds") in some spatial arrangement ("molecular structure"). No adiabatic hypothesis is made, and the analysis should hold for all bound states."

According to Essen's work, the motion of a particle in the molecule consists of three independent motions:

- The translational motion of the molecule as a whole
- The collective motion of the neutral subsystem
- The individual, internal motion in each "atom."

Individual motions of electrons and nuclei are not considered. The above classification allowed him to express coordinates of any particle in the molecule as

\[ r_i = R + r^C_{\gamma(i)} + r^I_i, \]  

where \( R \) defines the position of the molecular CM with respect to a stationary coordinate system, and \( \gamma(i) = \alpha \) if particle \( i \) belongs to the \( \alpha \)th composite subsystem. The vector \( r^C_{\gamma} \) is the CM vector of the subsystem \( \gamma \) relative to the molecular CM, while \( r^I_i \) is the internal position of the particle \( i \) relative to CM of the subsystem to which it belongs. Essen's work provides an essential conceptual study of the BO approximation.
To demonstrate some practical aspects of Essen’s theory, discussed also by Monkhorst [15], let us consider an \( N \)-particle system. In principle, one can reduce the \( N \)-body problem to an \( (N-1) \)-body problem by the CM elimination which is easily achieved by coordinate transformation. In all approaches the coordinates of the CM vector, \( \mathbf{R}_{CM} \), are defined as

\[
\mathbf{R}_{CM} = \frac{1}{M} \sum_{i=1}^{N} m_i \mathbf{r}_i, \tag{1.27}
\]

with

\[
M = \sum_{i=1}^{N} m_i. \tag{1.28}
\]

The remaining coordinates of the set are internal coordinates that can be defined with respect to CM as

\[
\rho_i = \mathbf{r}_i - \mathbf{R}_{CM}, \quad (i = 1, 2, ..., N). \tag{1.29}
\]

However, since

\[
\rho_N = -\frac{1}{m_N} \sum_{i=1}^{N-1} m_i \rho_i, \tag{1.30}
\]

the coordinates \( (\rho_1, ..., \rho_N, \mathbf{R}_{CM}) \) are linearly dependent.

One can avoid the linear dependence between internal coordinates by defining them with respect to any one of the \( N \) particles as suggested by Girardeau [47],

\[
\rho_i = \mathbf{r}_i - \mathbf{r}_N, \quad (i = 1, ..., N - 1). \tag{1.31}
\]

This is an extension of the coordinate transformation used for three particle systems. The set also includes the position vector of CM, \( \mathbf{R}_{CM} \). There are still other coordinate sets that can be used, for example polyspherical coordinates [45].

After separation of CM the next step involves variational solution of the internal eigenvalue problem. In practical realization one can encounter the problem that in some types of internal coordinates the kinetic energy part, or the potential energy part of the Hamiltonian may become excessively complicated due to additional terms resulting from the coordinate transformation. Also a problem may
arise in expressing the variational wave function using the internal coordinates and implementing the appropriate permutational properties. The problem is usually relatively minor for three- or four- particle problems. However, it can become more complicated when the size of the system grows.

Another interesting nonadiabatic approach to multiparticle systems known as the Generator Coordinate Method (GCM) has been proposed by Lathouwers and van Leuven [48,49]. The main idea of the GCM method is replacement of the nuclear coordinates in the BO electronic wave function by so called generator coordinates. The GCM represents conceptually an important approach in breaking with the BO approximation, unfortunately with little computational realization.

Finally, let us point out some common features of the nonadiabatic theory with the theory of highly excited rovibrational states, the theory of floppy molecules, the theory of molecular collisions, and the dynamics of Van der Waals complexes [45]. The starting point of considerations on such types of systems is the nuclear Hamiltonian,

$$\hat{H}_N = \sum_{i=1}^{N} \hat{T}_i + V(r_1, r_2, ..., r_N), \quad (1.32)$$

where the first term, expressed in terms of $3N$ nuclear coordinates, represents the kinetic energy, while the second term represents the potential hypersurface. Analogous to the nonadiabatic approaches discussed before, the separation of the translational degrees of freedom is accomplished by a coordinate transformation. The new internal coordinates are translation free [45,46]. The second step involves transformation from the space-fixed coordinates to body-fixed coordinates. After such a transformation the internal wave function, which is dependent on the $3N - 6$ translationally and rotationally invariant coordinates, is usually determined in a variational calculation. This wave function represents the internal vibrational motion of the molecule. The selection of an appropriate coordinate system represents one of the most difficult theoretical problems in attempts to solve Eq.(1.32). (The relevant discussion on this subject can be found in [46].)
CHAPTER II
NONADIABATIC MANY-BODY WAVE FUNCTION

2.1 INTRODUCTION

From the general considerations presented in the previous section one can expect that the many-body nonadiabatic wave function should fulfill the following conditions:

- all particles involved in the system should be treated equivalently,
- motion of all particles should be correlated at the same time,
- particles can be distinguished only via the permutational symmetry,
- the total wave function should reflect the internal and translational symmetry properties of the system,
- for fixed positions of nuclei the wave functions should become equivalent to what one obtains within the Born-Oppenheimer approximation,
- the wave function should be an eigenfunction of the appropriate spin and angular momentum operators.

The most general expansion which can facilitate fulfillment of the above conditions has the form

$$\Psi_{TOT} = \sum_{\mu=1}^{M} c_{\mu} P(1, 2, ..., N) |\omega_{\mu}(r_1, r_2, ..., r_N) \Theta_{S,M}^{N} \rangle,$$  \hspace{1cm} (2.1)

where $\omega_k$ and $\Theta_{S,M}^{N}$ represent the spatial and spin components respectively. In the above expansion, we schematically indicate that each $\omega_k$ should possess appro-
priate permutational properties, which is accomplished via an appropriate form of the permutation operator \(P(1, 2, ..., N)\). The total wave function should be also an eigenfunction of the \(\hat{S}^2\) and \(\hat{S}_z\) spin operators which is accomplished by an appropriate form of the spin wave function \(\Theta_{S,M}^N\). Relativistic and spin-orbit effects are neglected.

Different functional bases have been proposed for nonadiabatic calculations on three-body systems, however extension to many particles has been difficult for the following reason: Due to the nature of the Coulombic two-body interactions the spatial correlation should be included explicitly in the wave function, \(i.e.,\), inter-particle distances should be incorporated in the basis functions. Unfortunately, for most types of the explicitly correlated wave functions the resulting many-electron integrals are usually difficult to evaluate. An exception is the basis set of explicitly correlated Gaussian geminals which contain products of two Gaussian orbitals and a correlation factor of the form \(\exp(-\beta r_{ij}^2)\). These functions were introduced by Boys [50] and Singer [51]. The correlation part effectively creates a Coulomb hole, \(i.e.,\), reduces or enhances the amplitude of the wave function when two particles approach one another. The application of the explicitly correlated Gaussian geminals is not as effective as other types of correlated functions due to a rather poor representation of the cusp. However, such functions form a mathematically complete set [52], and all required integrals have closed forms as was demonstrated by Lester and Kraus [53]. During the last three decades explicitly correlated Gaussian geminals have been successfully applied to different problems as, for example, in the calculations of the correlation energy for some closed-shell atoms and molecules, intermolecular interaction potentials, polarizabilities, Compton profiles, and electron scattering cross sections [54-61]. Explicitly correlated Gaussian geminals were also applied to minimize the second-order energy functional. First, Pan and King [62] demonstrated that rather short expansions with appropriate minimizations of nonlinear parameters lead to very accurate results for atoms. The same idea was later extended to molecular systems by Adamowicz and Sadlej [63-69]. We should also mention a series of papers by Monkhorst and co-workers [70-74] where explicitly correlated Gaussian geminals were used in conjunction with the second order
perturbation theory as well as the coupled cluster method.

In the remainder of this section we would like to describe an application of
the explicitly correlated Gaussian-type functions to nonadiabatic calculations on a
multipartile system. The explicitly correlated Gaussian functions form a convenient
basis set for multiparticle nonadiabatic calculations because, due to the separability
of the squared coordinates, the integrals over Gaussian functions are relatively easy
to evaluate. As a consequence, one can afford to use a larger number of these
functions in the basis set than in cases of explicitly correlated functions of other
types.

In a nonadiabatic calculation the spatial part of the \(N\)-particle wave function
(2.1) is expanded in terms of explicitly correlated Gaussian functions (which will be
called Gaussian cluster functions)

\[
\omega_k = \exp \left( -\sum_{i=k}^{N} \alpha_k^i |\mathbf{r}_i - \mathbf{R}_k^j|^2 - \sum_{i=1}^{N} \sum_{j>i}^{N} \beta_{ij}^k |\mathbf{r}_i - \mathbf{r}_j|^2 \right),
\]

where the vector \(\mathbf{r}\) is equal to

\[
\mathbf{r} = (r_1, r_2, ..., r_N),
\]

and \(\mathbf{r}^T\) is its transpose. The matrix \(\mathbf{B}^k\) is constructed with the use the correlation
exponents \((\beta_{ii}^k = 0)\)

\[
\mathbf{B}^k = \begin{pmatrix}
\sum_{j=1}^{N} \beta_{1j}^k & -\beta_{12}^k & \cdots & -\beta_{1N}^k \\
-\beta_{12}^k & \sum_{j=1}^{N} \beta_{2j}^k & \cdots & -\beta_{2N}^k \\
\vdots & \vdots & \ddots & \vdots \\
-\beta_{1N}^k & -\beta_{2N}^k & \cdots & \sum_{j=1}^{N} \beta_{Nj}^k
\end{pmatrix}.
\]
2.2 BASIC PROPERTIES OF SPHERICAL GAUSSIAN ORBITALS

This paragraph introduces the basic concepts of Gaussian basis set functions. From a mathematical point of view many different kinds of basis set functions could be used. Only two types of basis functions have found common use, i.e., Slater-type functions and Gaussian-type functions. The s-type unnormalized Slater-type function, centered at $\mathbf{R}$, has the form

$$\chi(\zeta, \mathbf{r} - \mathbf{R}) = \exp(-\zeta|\mathbf{r} - \mathbf{R}|),$$

where $\zeta$ is the Slater orbital exponent. The s-type unnormalized Gaussian-type function, centered at $\mathbf{R}$, has the form

$$g(\alpha, \mathbf{r} - \mathbf{R}) = \exp(-\alpha|\mathbf{r} - \mathbf{R}|^2),$$

where $\alpha$ is the Gaussian orbital exponent. The major differences between the two functions occurs at $r = 0$ and at large $r$. At $r = 0$, the Slater function has a finite slope

$$\left(\frac{d}{dr} e^{-\zeta r}\right)_{r=0} \neq 0,$$

and the Gaussian function has a zero slope,

$$\left(\frac{d}{dr} e^{-\alpha r^2}\right)_{r=0} = 0.$$  \hspace{1cm} (2.9)

For large values of $r$, the Gaussian function decays much more rapidly than the Slater function.

In electronic structure calculations, the Slater-type functions more correctly describe the features of the molecular orbitals than the Gaussian-type functions. However, the majority of large-scale molecular electronic structure calculations in modern quantum chemistry are performed using Gaussian-type functions. The reason why the Gaussian functions are more frequently used in quantum mechanical calculations, than Slater functions, is the fact that molecular integrals over Gaussian functions are relatively easy to evaluate, while integrals with Slater basis functions are difficult and time-consuming. This is due to the fact that product of two 1s
Gaussian functions, each on a different centers, is a 1s Gaussian function on a third center times a constant. Let us consider two spherical Gaussians, the first centered at $\mathbf{R}^{\mu}$

$$g(\alpha^{\mu}, \mathbf{r} - \mathbf{R}^{\mu}) = \exp(-\alpha^{\mu}|\mathbf{r} - \mathbf{R}^{\mu}|^2),$$

and the second at $\mathbf{R}^{\nu}$

$$g(\alpha^{\nu}, \mathbf{r} - \mathbf{R}^{\nu}) = \exp(-\alpha^{\nu}|\mathbf{r} - \mathbf{R}^{\nu}|^2),$$

respectively. The product of two Gaussian functions is proportional to a Gaussian centered on $\mathbf{R}^{\mu\nu}$

$$g(\alpha^{\mu}, \mathbf{r} - \mathbf{R}^{\mu})g(\alpha^{\nu}, \mathbf{r} - \mathbf{R}^{\nu}) = K_{\mu\nu} \exp \left(-\alpha^{\mu\nu}|\mathbf{r} - \mathbf{R}^{\mu\nu}|^2 \right),$$

where the factor $K_{\mu\nu}$ is an exponential function of two centers

$$K_{\mu\nu} = \exp \left(-\frac{\alpha^{\mu\nu}}{\alpha^{\mu\nu}}|\mathbf{R}^{\mu} - \mathbf{R}^{\nu}|^2 \right),$$

and $\alpha^{\mu\nu} = \alpha^{\mu} + \alpha^{\nu}$. The position of the third center is defined as follows

$$\mathbf{R}^{\mu\nu} = \frac{\alpha^{\mu}\mathbf{R}^{\mu} + \alpha^{\nu}\mathbf{R}^{\nu}}{\alpha^{\mu\nu}}.$$

The above property simplifies evaluation of molecular integrals. In the next section, the derivation will be demonstrated.

### 2.3 Molecular Integrals Over Spherical Gaussians

This section is devoted to the summarization of molecular integrals over spherical Gaussians. The contraction properties of the Gaussian functions mentioned in the previous section considerably simplify evaluation of molecular integrals. The two-center overlap integral ($OV$), for example, can be immediately calculated using this property as follows

$$OV =$$
\[ \int g(\alpha^\nu, r - R^\nu)g(\alpha^\nu, r - R^\nu)dr = K_{\mu \nu} \int \exp \left( -a^{\mu \nu}|r - R^{\mu \nu}|^2 \right) dr. \] (2.15)

The integration over \( r \) coordinate can be easily carried out to find the result
\[
\int \exp \left( -a^{\mu \nu}|r - R^{\mu \nu}|^2 \right) dr = \left( \frac{\pi}{a^{\mu \nu}} \right)^{\frac{3}{2}},
\] (2.16)
and the overlap integral becomes
\[
\langle g(\alpha^\mu, r - R^\mu)|g(\alpha^\nu, r - R^\nu) \rangle = K_{\mu \nu} \left( \frac{\pi}{a^{\mu \nu}} \right)^{\frac{3}{2}}. \] (2.17)

The kinetic energy integral \((KE)\)
\[
KE = \int g(\alpha^\mu, r - R^\mu) \left( -\frac{1}{2} \nabla^2 \right) g(\alpha^\nu, r - R^\nu) dr
\] (2.18)
can be obtained in similar way as the overlap integral, \(i.e.,\) by direct differentiation and integration. The same result can be obtained using a slightly different technique. This technique will be later applied to evaluate multiparticle integrals with explicitly correlated Gaussian functions. To demonstrate the major transformation involved in the integration let us consider the following integral
\[
I^{\mu \nu} = \int \nabla g(\alpha^\mu, r - R^\mu)[\nabla g(\alpha^\nu, r - R^\nu)] dr.
\] (2.19)

Differentiating both Gaussian orbitals and using the Gaussian contraction theorem, \(I^{\mu \nu}\) becomes
\[
I^{\mu \nu} = 4\alpha^\mu \alpha^\nu K_{\mu \nu} \times
\int \left( r^2 - r \cdot R^\mu - r \cdot R^\nu + R^\mu \cdot R^\nu \right) \exp \left( -a^{\mu \nu}|r - R^{\mu \nu}|^2 \right) dr. \] (2.20)

Further simplification can be made by using Eq.(2.16) to find the result
\[
I^{\mu \nu} = 4\alpha^\mu \alpha^\nu K_{\mu \nu} \int r^2 \exp \left( -a^{\mu \nu}|r - R^{\mu \nu}|^2 \right) dr
\]
\[
- 4\alpha^\mu \alpha^\nu K_{\mu \nu}(R^\mu + R^\nu) \cdot \int r \exp \left( -a^{\mu \nu}|r - R^{\mu \nu}|^2 \right) dr
\]
\[
+ 4\alpha^\mu \alpha^\nu (R^\mu \cdot R^\nu) \langle g(\alpha^\mu, r - R^\mu)|g(\alpha^\nu, r - R^\nu) \rangle
\] (2.21)

In order to evaluate the last integral let us consider the result of differentiation of the spherical Gaussian \(g(\alpha^{\mu \nu}, r - R^{\mu \nu})\) with respect to orbital exponent \(a_{\mu \nu}\)
\[-\frac{\partial}{\partial a^\mu} \int \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr = \int r^2 \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr\]

\[-2R^{\mu\nu} \cdot \int r \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr\]

\[+ (R^{\mu\nu})^2 \int \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr, \quad (2.22)\]

which together with formula (2.16) becomes

\[-\frac{\partial}{\partial a^\mu} \left( \frac{\pi}{a^\mu} \right)^{\frac{3}{2}} = \int r^2 \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr\]

\[-2R^{\mu\nu} \cdot \int r \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr + (R^{\mu\nu})^2 \left( \frac{\pi}{a^\mu} \right)^{\frac{3}{2}}. \quad (2.23)\]

Taking $a^{\mu\nu}$ as an independent variable, the expression for $I^{\mu\nu}$ together with Eq.(2.23) gives the result

\[I^{\mu\nu} = -4a^{\mu\nu} \frac{\partial}{\partial a^\mu} \left( g(\alpha^\mu, r - R^\mu) |g(\alpha^\nu, r - R^\nu)\right)\]

\[+ 4\alpha^\mu \alpha^\nu [R^\mu \cdot \nabla^\nu - (R^{\mu\nu})^2] \left( g(\alpha^\mu, r - R^\mu) |g(\alpha^\nu, r - R^\nu)\right)\]

\[- 4\alpha^\mu \alpha^\nu K_{\mu\nu}[R^\mu + R^\nu + 2R^{\mu\nu}] \cdot \int r \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr. \quad (2.24)\]

The last integral in the above formula can be easily evaluated to find

\[\int r \exp \left( -a^{\mu\nu}|r - R^{\mu\nu}|^2 \right) dr = R^{\mu\nu} \left( \frac{\pi}{a^\mu} \right)^{\frac{3}{2}}, \quad (2.25)\]

and finally Eq.(2.24) becomes

\[I^{\mu\nu} = -4a^{\mu\nu} \frac{\partial}{\partial a^\mu} \left( g(\alpha^\mu, r - R^\mu) |g(\alpha^\nu, r - R^\nu)\right)\]

\[+ 4\alpha^\mu \alpha^\nu \frac{\alpha^\mu + \alpha^\nu}{\alpha^\mu + \alpha^\nu} [R^\mu - R^\nu]^2 \left( g(\alpha^\mu, r - R^\mu) |g(\alpha^\nu, r - R^\nu)\right). \quad (2.26)\]

The expression for the kinetic energy integral,

\[\langle g(\alpha^\mu, r - R^\mu) | - \frac{1}{2} \nabla^2 |g(\alpha^\nu, r - R^\nu)\rangle = \frac{1}{2} I^{\mu\nu}, \quad (2.27)\]
can be now easily expressed in terms of the overlap integrals.

Evaluation of nuclear attraction and two electron repulsion integrals require more advanced mathematical technique known as the Fourier transform method. The technique is based on replacing each function in the integrand by its Fourier transform. For a given function \( f(r) \) its three-dimensional Fourier transform is defined by

\[
F(k) = \int f(r) \exp(-i \mathbf{k} \cdot \mathbf{r}) \, dr
\]

where the vector \( \mathbf{k} \) is the transform variable. The Fourier integrals theorem reads

\[
f(r) = (2\pi)^{-3} \int F(k) \exp(+i \mathbf{k} \cdot \mathbf{r}) \, dk
\]

and \( F(k) \) and \( f(r) \) are a Fourier transform pair. Particularly, for \( \frac{1}{r} \) the Fourier transform is \( \frac{4\pi}{k^2} \), while for \( \exp(-\alpha r^2) \) it is \( \left( \frac{2\pi}{\alpha} \right)^\frac{3}{2} \exp(-k^2/4\alpha) \). The Fourier representation of the three-dimensional Dirac delta function is

\[
\delta(r_1 - r_2) = (2\pi)^{-3} \int \exp(+i \mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)) \, dk
\]

Having discussed the basic elements of the Fourier transform theory, let us consider the nuclear attraction integral \( (NA) \) involving two spherical Gaussian functions. After contracting two Gaussian functions into one Gaussian

\[
NA = \int g(\alpha^\mu, \mathbf{r} - \mathbf{R}^\mu) \frac{1}{|\mathbf{r} - \mathbf{R}_c|} g(\alpha^\nu, \mathbf{r} - \mathbf{R}^\nu) \, dr
\]

\[
= K_{\mu\nu} \int \exp \left( -a^{\mu\nu}|\mathbf{r} - \mathbf{R}^{\mu\nu}|^2 \right) \frac{1}{|\mathbf{r} - \mathbf{R}_c|} \, dr,
\]

and by replacing both terms in the integral by their Fourier transforms one obtains

\[
NA = K_{\mu\nu} (2\pi)^{-6} \left( \frac{\pi}{a_{\mu\nu}} \right)^\frac{3}{2} \times
\]

\[
\int \int \exp(-k_1^2/4a_{\mu\nu}) \exp[i\mathbf{k}_1 \cdot (\mathbf{r} - \mathbf{R}^{\mu\nu})] \times
\]

\[
4\pi k_2^{-2} \exp[i\mathbf{k}_2 \cdot (\mathbf{r} - \mathbf{R}_c)] \, d\mathbf{k}_1 d\mathbf{k}_2.
\]

The terms in the last integral can be rearranged to obtain the result

\[
NA = 4\pi K_{\mu\nu} (2\pi)^{-6} \left( \frac{\pi}{a_{\mu\nu}} \right)^\frac{3}{2} \times
\]
\[
\int \int \int k_1^{-2} \exp(-k_1^2/4\alpha_{\mu\nu}) \exp(-ik_1 \cdot R_{\mu\nu}) \exp(-ik_2 \cdot R_c) \times \exp[i\mathbf{r} \cdot (k_1 + k_2)] dr dk_1 dk_2. \tag{2.33}
\]

Integration over the \( r \) coordinate introduces the Dirac delta function given by Eq.\( (2.30) \)
\[
NA = 4\pi K_{\mu\nu}(2\pi)^{-3} \left( \frac{\pi}{\alpha_{\mu\nu}} \right)^{3/2} \times 
\int \int k_2^{-2} \exp(-k_2^2/4\alpha_{\mu\nu}) \exp(-ik_2 \cdot R_{\mu\nu}) \times \exp(-ik_2 \cdot R_c) \delta(k_1 + k_2) dk_1 dk_2. \tag{2.34}
\]

With the use of the following property of the Dirac delta function
\[
\int \delta(r_1 - r_2)f(r_1)dr_1 = f(r_2), \tag{2.35}
\]
the expression for the nuclear attraction integral becomes
\[
NA = K_{\mu\nu}(2\pi)^{3/2} \times 
\left( \frac{\pi}{\alpha_{\mu\nu}} \right)^{3/2} \int \exp[-k^2/4\alpha_{\mu\nu}]k^{-2} \exp(-i\mathbf{k} \cdot (\mathbf{R}_{\mu\nu} - \mathbf{R}_c))dk. \tag{2.36}
\]

Usually, the last integral is expressed in terms of the incomplete gamma function
\[
F_0(t) = t^{-1/2} \int_0^{t^{1/2}} \exp(-y^2)dy, \tag{2.37}
\]
and becomes
\[
\langle g(\alpha^\mu, \mathbf{r} - \mathbf{R}^\mu)|\frac{1}{|\mathbf{r} - \mathbf{R}_c|}|g(\alpha^\nu, \mathbf{r} - \mathbf{R}^\nu)\rangle = \frac{2\pi}{\alpha_{\mu\nu}} K_{\mu\nu} F_0(\alpha_{\mu\nu}|\mathbf{R}_{\mu\nu} - \mathbf{R}_c|). \tag{2.38}
\]

The last integral which will be considered in this section is the two-electron integral
\[
ER = \int \int g(\alpha_1^\mu, \mathbf{r}_1 - \mathbf{R}_1^\mu)g(\alpha_2^\mu, \mathbf{r}_2 - \mathbf{R}_2^\mu) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \times 
g(\alpha_1^\nu, \mathbf{r}_1 - \mathbf{R}_1^\nu)g(\alpha_2^\nu, \mathbf{r}_2 - \mathbf{R}_2^\nu) dr_1 dr_2. \tag{2.39}
\]

After application of the contraction theorem for Gaussian orbitals the \( ER \) integral becomes
\[
ER = K_{\mu\nu}^{(2)} \times
\]
\[ \int \int \exp(-a_1^{\mu \nu} |r_1 - R_1^{\mu \nu}|^2) \frac{1}{|r_1 - r_2|} \exp(-a_2^{\mu \nu} |r_2 - R_2^{\mu \nu}|^2) dr_1 dr_2, \]  
(2.40)

where the definition of the exponential factor \( K_{\mu \nu} \) was extended in the following way

\[ K_{\mu \nu}^{(2)} = \exp \left( - \sum_{i=1}^{2} \frac{\alpha_i^{\mu} \alpha_i^{\nu}}{\alpha_i^{\mu} + \alpha_i^{\nu}} |R_i^{\mu} - R_i^{\nu}|^2 \right). \]  
(2.41)

The procedure for evaluating this integral is similar to the one applied for the \( NA \) integral. Replacing the three terms in the integrand by their Fourier transforms gives

\[ ER = K_{\mu \nu}^{(2)} (2\pi)^{-9} \int \int \int \int \left( \frac{\pi}{a_1^{\mu \nu} a_2^{\mu \nu}} \right)^{\frac{3}{2}} \exp(-k_1^2/4a_1^{\mu \nu}) \exp[i k_1 \cdot (r_1 - R_1^{\mu \nu})] \]  
\[ \times 4\pi k_2^{-2} \exp[i k_2 \cdot (r_1 - r_2)] \]  
\[ \times \left( \frac{\pi}{a_2^{\mu \nu}} \right)^{\frac{3}{2}} \exp(-k_3^2/4a_2^{\mu \nu}) \exp[i k_3 \cdot (r_2 - R_2^{\mu \nu})] dr_1 dr_2 dk_1 dk_2 dk_3. \]  
(2.42)

After grouping together the exponential terms dependent on the variables \( r_1 \) and \( r_2 \) we get

\[ ER = 4\pi K_{\mu \nu}^{(2)} (2\pi)^{-9} \left( \frac{\pi^2}{a_1^{\mu \nu} a_2^{\mu \nu}} \right)^{\frac{3}{2}} \int \int \int \int \exp(-k_1^2/4a_1^{\mu \nu}) \exp(-k_3^2/4a_2^{\mu \nu}) k_2^{-2} \]  
\[ \times \exp(-i k_1 \cdot R_1^{\mu \nu}) \exp(-i k_3 \cdot R_2^{\mu \nu}) \exp[i r_1 \cdot (k_1 + k_2)] \]  
\[ \times \exp[i r_2 \cdot (k_3 - k_2)] dr_1 dr_2 dk_1 dk_2 dk_3. \]  
(2.43)

The integration over \( r_1 \) and \( r_2 \) introduces two Dirac delta functions

\[ ER = 4\pi K_{\mu \nu}^{(2)} (2\pi)^{-3} \left( \frac{\pi^2}{a_1^{\mu \nu} a_2^{\mu \nu}} \right)^{\frac{3}{2}} \int \int \int \exp(-k_1^2/4a_1^{\mu \nu}) \exp(-k_3^2/4a_2^{\mu \nu}) k_2^{-2} \times \]  
\[ \exp(-i k_1 \cdot R_1^{\mu \nu}) \exp(-i k_3 \cdot R_2^{\mu \nu}) \delta(k_1 + k_2) \delta(k_3 - k_2) dr_1 dr_2 dk_1 dk_2 dk_3. \]  
(2.44)

We can now set \( k_1 = -k_2 \) and \( k_3 = k_2 \) and relabel \( k_2 \) as \( k \) to obtain

\[ ER = K_{\mu \nu}^{(2)}/(2\pi) \left( \frac{\pi^2}{a_1^{\mu \nu} a_2^{\mu \nu}} \right)^{\frac{3}{2}} \]  
\[ \times \int k^{-2} \exp[-(a_1^{\mu \nu} + a_2^{\mu \nu}) k^2/4] \exp[i k \cdot (R_1^{\mu \nu} - R_2^{\mu \nu})]. \]  
(2.45)
The final form of the two electron integral can also be expressed in terms of the incomplete gamma function to yield the final formula

\[
\langle g(\alpha_1^\mu, r_1 - R_1^\mu) g(\alpha_2^\nu, r_2 - R_2^\nu) \rangle = \frac{1}{|r_1 - r_2|} g(\alpha_1^\nu, r_1 - R_1^\nu) g(\alpha_2^\nu, r_2 - R_2^\nu) =
\]

\[
\frac{2\pi^{5/2} K_2^{(2)}}{a_1^{\mu\nu} a_2^{\mu\nu} \sqrt{(a_1^{\mu\nu} + a_2^{\mu\nu})}} F_0 \left( \frac{a_1^{\mu\nu} a_2^{\mu\nu}}{a_1^{\mu\nu} + a_2^{\mu\nu}} |R_1^{\mu\nu} - R_2^{\mu\nu}|^2 \right). \tag{2.46}
\]

This formula for the electron-repulsion integral concludes the summary of molecular integrals over spherical Gaussians.

### 2.4 MANY PARTICLE INTEGRALS

In this section we would like to discuss evaluation of many particle integrals over explicitly correlated Gaussian functions which are required for our method of nonadiabatic calculations. The simplicity of the appropriate algorithms for molecular integrals leading to efficient computation implementations represents one of the most important elements in the development of our multiparticle nonadiabatic methodology. The integral procedures are quite general and can be extended to an arbitrary number of particles. To avoid unnecessary details we will first demonstrate the general strategy for calculating integrals with spherical Gaussians. Next we will discuss how the procedure can be extended to Gaussians with higher angular momenta.

Let us consider a general matrix element containing two Gaussian cluster functions \( \langle \omega_\mu | \hat{O} | \omega_\nu \rangle \), where \( \hat{O} \) represents a one-body operator \( \hat{O}(i) \), or a two-body operator \( \hat{O}(i,j) \) (omitted from the present discussion is the kinetic energy integral and operators containing differentiation which will be described later).

\[
\langle \omega_\mu (r_1, r_2, ..., r_N) | \hat{O} | \omega_\nu (r_1, r_2, ..., r_N) \rangle
= \int \int \ldots \int \exp \left( -\sum_{n=1}^{N} \alpha_n^{\mu} |r_n - R_n^{\mu}|^2 - r B^\nu r^T \right)
\]
The strategy of calculating the above integral is the following: we perform integration over all coordinates except \( r_i \) and \( r_j \) in the case of the two-body operator, \( \hat{O}(i,j) \), and all coordinates except \( r_i \) in the case of the one-body operator, \( \hat{O}(i) \). First we will demonstrate the integration over two arbitrary coordinates, \( r_p \) and \( r_q \) \((p, q \neq i, j)\) and then using mathematical induction procedure we will demonstrate how the integration can be accomplished for an arbitrary number of particles. The kinetic energy integral is an exception and cannot be reduced by direct integration over the coordinates of the particles which are not involved in the operator. The reason is that the correlation factors which couple all electrons with the electron in the kinetic energy operator occur on both sides of the operator and cannot be combined as easily as for a multiplicative operator. In the next section kinetic energy integral will be calculated using a slightly different technique.

In general, the multiparticle integral (2.47) is a many-center integral. In order to evaluate this integral we first use the contraction theorem for products of Gaussian orbitals introduced in the previous section with the center \( \mathbf{R}_n^{\mu\nu} \) defined as follows,

\[
\mathbf{R}_n^{\mu\nu} = \frac{\alpha_n^\mu \mathbf{R}_n^\mu + \alpha_n^\nu \mathbf{R}_n^\nu}{\alpha_n^\mu + \alpha_n^\nu},
\]

so that the integral (2.47) takes the form

\[
\langle \omega_\mu | \hat{O} | \omega_\nu \rangle = K_{\mu\nu} \times 

\int \ldots \int \hat{O} \exp \left( - \sum_{n=1}^{N} \alpha_n^{\mu\nu} |\mathbf{r}_n - \mathbf{R}_n^{\mu\nu}|^2 - \mathbf{r} \mathbf{B}^{\mu\nu} \mathbf{r}^T \right) d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N,
\]

where the factor \( K_{\mu\nu} \) is an exponential function of all centers

\[
K_{\mu\nu} = \exp \left( - \sum_{n=1}^{N} \frac{\alpha_n^\mu \alpha_n^\nu}{\alpha_n^\mu + \alpha_n^\nu} |\mathbf{R}_n^\mu - \mathbf{R}_n^\nu|^2 \right).
\]

For simplicity and compactness of the notation we used the abbreviation \( a_n^{\mu\nu} = \alpha_n^\mu + \alpha_n^\nu \), and \( \mathbf{B}^{\mu\nu} = \mathbf{B}^\mu + \mathbf{B}^\nu \). Let us also rewrite the last integral in a slightly different way and explicitly separate the \( G(\mathbf{r}_i, \mathbf{r}_j) \) function

\[
\langle \omega_\mu | \hat{O} | \omega_\nu \rangle = K_{\mu\nu} \times 

\int \ldots \int \hat{O} \exp \left( - \sum_{n=1}^{N} \frac{\alpha_n^\mu \alpha_n^\nu}{\alpha_n^\mu + \alpha_n^\nu} |\mathbf{R}_n^\mu - \mathbf{R}_n^\nu|^2 \right) G(\mathbf{r}_i, \mathbf{r}_j) d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N.
\]
\[ \int \int \hat{O}(i,j) G(r_i, r_j) \exp \left(-a_i^{\mu\nu} |r_i - R_i^{\mu\nu}|^2\right) \exp \left(-a_j^{\mu\nu} |r_j - R_j^{\mu\nu}|^2\right) \, dr_i \, dr_j. \]  

(2.51)

The \( G(r_i, r_j) \) function contains all information about the correlation part and is defined as follows

\[ G(r_i, r_j) = \int \int \ldots \int \exp \left(- \sum_{n=1}^{N} a_n^{\mu\nu} |r_n - R_n^{\mu\nu}|^2 - r B^{\mu\nu} r^T\right) \, dr_1 \, dr_2 \ldots \, dr_N / (i,j), \]  

(2.52)

where \((i,j)\) indicates that we do not integrate over the coordinates of the \(i\)-th and \(j\)-th particles. It should be also pointed out that if the elements of the correlation matrix \( B^{\mu\nu} \) are equal to zero the \( G \) function becomes simply a product of the overlap integrals between Gaussian orbitals. Evaluation of the \( G(r_i, r_j) \) concludes the reduction when \( \hat{O} \) is a two-body operator. In the one-body case we additionally integrate the \( G \) function over the \( r_j \) coordinate, \( G(r_i) = \int G(r_i, r_j) \, dr_j \). As it is demonstrate in the Appendix A, this function has the following form for \( N \) particles

\[ G(r_i, r_j) = \pi \frac{2^{(N-2)}}{2} \left[ \det(A^{\mu\nu} + B^{\mu\nu}; i, j)\right]^{-\frac{3}{2}} \times \]

\[ \exp \left[ -\frac{1}{\det(A^{\mu\nu} + B^{\mu\nu}; i, j)} \times \right] \]

\[ \left( R_i^{\mu\nu}, \ldots, R_N^{\mu\nu}; i, j\right) S(1, \ldots, N; i, j)(R_1^{\mu\nu}, \ldots, R_N^{\mu\nu}; i, j)^T \right] \times \]

\[ \exp \left( -b_{ii}^{(N-2)} r_i^2 - b_{jj}^{(N-2)} r_j^2 - 2b_{ij}^{(N-2)} r_i r_j \right) \times \]

\[ \exp \left[ -\frac{2}{\det(A^{\mu\nu} + B^{\mu\nu}; i, j)} \times \right] \]

\[ \left[ r_i \sum_{n=1}^{N-2} a_n^{\mu\nu} b_{in}^{(N-3)} R_i^{\mu\nu} + r_j \sum_{n'=1}^{N-2} a_{n'}^{\mu\nu} b_{jn'}^{(N-3)} R_n^{\mu\nu} \right]. \]  

(2.53)

with abbreviations introduced in the appendix. Having discussed the scheme of the reduction we may now relatively easily find formulas for the elementary integrals and finally calculate the multiparticle molecular integrals. Before we present the required
integrals it should be mentioned that formulas for two and three particle integrals with Gaussian geminals were given by Lester and Krauss [53]. Also Boys [50] and Singer [51] demonstrated some ideas on how those types of integrals can be evaluated. The elementary integrals for the Gaussian geminals can be calculated using the convolution theorem as it was originally presented by Lester and Krauss, but this theorem is not so easily applicable when more than two particles are correlated at the same time. Our contribution is to present formulas for integrals over an arbitrary number of particles in a form similar to what one has for the Gaussian orbitals. This enables an effective practical implementation of the derived formalism. Indeed, as we will see later, the final integrals have essentially the same structure as the integrals with Gaussians orbitals, due to the "internal symmetry", but, of course, our expressions contain more complicated combinations of the exponential parameters and the coordinates of the orbital centers.

First, let us consider the simplest case i.e. the overlap integral. Let us introduce the square diagonal matrix \( A^{\mu\nu} \), where the p-th diagonal element is simply \( a^p_{\mu\nu} \). Using Eq.(2.53) we find

\[
\langle \omega_{\mu}(r_1, r_2, ..., r_N) | \omega_{\nu}(r_1, r_2, ..., r_N) \rangle = \pi^{N/2} K_{\mu\nu}[\text{det}(A + B^{\mu\nu})]^{-\frac{N}{2}} \times
\exp \left[ -\frac{1}{\text{det}(A^{\mu\nu} + B^{\mu\nu})} (R^{\mu\nu}_1, ..., R^{\mu\nu}_N) S (1, ..., N) (R^{\mu\nu}_1, ..., R^{\mu\nu}_N)^T \right].
\]

The similarity of this integral and the overlap integral for Gaussian orbitals is evident.

The next integral is the nuclear attraction integral. By performing a reduction over all coordinates except the \( r_i \) coordinate, the elementary integral becomes

\[
\langle \omega_{\mu}(r_1, r_2, ..., r_N) | \frac{1}{|r_i - R_e|} | \omega_{\nu}(r_1, r_2, ..., r_N) \rangle = \pi^{\frac{3(N-1)}{2}} K_{\mu\nu}[\text{det}(A^{\mu\nu} + B^{\mu\nu}; i)]^{-\frac{3}{2}} \times
\exp \left[ -\frac{1}{\text{det}(A^{\mu\nu} + B^{\mu\nu}; i)} (R^{\mu\nu}_1, ..., R^{\mu\nu}_N; i) S (1, ..., N; i) (R^{\mu\nu}_1, ..., R^{\mu\nu}_N; i)^T \right] \times
\int \frac{1}{|r_i - R_e|} \exp \left( -c_{i\mu\nu} |r_i - R_i^{\mu\nu}|^2 - b_{ii}^{(N-1)} r_i^2 - 2r_i X_{i\mu\nu} \right) dr_i,
\]

(2.55)
with
\[ X_i^{\mu \nu} = \frac{1}{\det(A^{\mu \nu} + B^{\mu \nu}; i)} \sum_{n=1}^{N-1} a_n^{\mu \nu} a_0^{(N-2)} R_n^{\mu \nu}. \] (2.56)

In the last formula we used similar notation as in the previous section. Index \( i \) after the semicolon denotes that the corresponding term does not contain elements with subscript \( i \). The last integral in Eq.(2.55) may be rewritten in a more convenient form as
\[
\int \frac{1}{|r_i - R_c|} \exp \left( -a_i^{\mu \nu} |r_i - R_i^{\mu \nu}|^2 - b_i^{(N-1)} r_i^2 \right) dr_i =
\exp \left[ \frac{(a_i^{\mu \nu} R_i^{\mu \nu} - X_i^{\mu \nu})^2}{a_i^{\mu \nu} + b_i^{(N-1)}} \right] \exp \left[ -a_i^{\mu \nu} (R_i^{\mu \nu})^2 \right] \times
\int \frac{1}{|r_i - R_c|} \exp \left[ -(a_i^{\mu \nu} + b_i^{(N-1)}) \left| r_i - \frac{a_i^{\mu \nu} R_i^{\mu \nu} - X_i^{\mu \nu}}{a_i^{\mu \nu} + b_i^{(N-1)}} \right|^2 \right] dr_i. \] (2.57)

Using the above result the nuclear attraction integral can be rewritten in terms of the error function as
\[
\langle \omega_\mu(r_1, r_2, ..., r_N) \rangle = \frac{1}{|r_i - R_c|} |\omega_\nu(r_1, r_2, ..., r_N)| =
\pi^{\frac{3(N-1)}{2}} K_{\mu \nu} [\det(A^{\mu \nu} + B^{\mu \nu}; i)]^{-\frac{3}{2}} \times
\exp \left[ -\frac{1}{\det(A^{\mu \nu} + B^{\mu \nu}; i)} \left( R_1^{\mu \nu}, ..., R_N^{\mu \nu}; i \right) S(1, ..., N; i)(R_1^{\mu \nu}, ..., R_N^{\mu \nu}, i)T \right] \times
\left( \frac{2\pi}{a_i^{\mu \nu} + b_i^{(N-1)}} \right) \exp \left[ \frac{(a_i^{\mu \nu} R_i^{\mu \nu} - X_i^{\mu \nu})^2}{a_i^{\mu \nu} + b_i^{(N-1)}} - a_i^{\mu \nu} (R_i^{\mu \nu})^2 \right] \times
F_0 \left[ (a_i^{\mu \nu} + b_i^{(N-1)}) \left| \frac{a_i^{\mu \nu} R_i^{\mu \nu} - X_i^{\mu \nu}}{a_i^{\mu \nu} + b_i^{(N-1)}} - R_c \right|^2 \right]. \] (2.58)

The last integral which can be evaluated using the method described in this section is the electron repulsion integral. The two-electron integral after the reduction takes the form
\[
\langle \omega_\mu(r_1, r_2, ..., r_N) \rangle = \frac{1}{|r_i - r_j|} |\omega_\nu(r_1, r_2, ..., r_N)| =
\pi^{\frac{3(N-2)}{2}} K_{\mu \nu} [\det(A^{\mu \nu} + B^{\mu \nu}; i, j)]^{-\frac{3}{2}} \times
\]
\[
\exp \left[ -\frac{1}{\det(A^{\mu\nu} + B^{\mu\nu}; i, j)} \right] \times (R_i^{\mu\nu}, \ldots, R_N^{\mu\nu}; i, j) S(1, \ldots, N; i, j) (R_1^{\mu\nu}, \ldots, R_N^{\mu\nu}; i, j)^T \right] \times
\langle \omega_\mu(r_i, r_j) | \frac{1}{|r_i - r_j|} | \omega_\nu(r_i, r_j) \rangle,
\tag{2.59}
\]

where

\[
\langle \omega_\mu(r_i, r_j) | \frac{1}{|r_i - r_j|} | \omega_\nu(r_i, r_j) \rangle = \int \int \frac{1}{|r_i - r_j|} \exp \left( -a_i^{\mu\nu} |r_i - R_i^{\mu\nu}|^2 - a_j^{\mu\nu} |r_j - R_j^{\mu\nu}|^2 
- b_i^{(N-2)} r_i^2 - b_j^{(N-2)} r_j^2 - 2b_{ij}^{(N-2)} r_i r_j 
- \frac{2}{\det(A^{\mu\nu} + B^{\mu\nu}; i, j)} \times 
\left[ r_i \sum_{n=1}^{N-2} a_n^{\mu\nu} b_i^{(N-3)} R_n^{\mu\nu} + r_j \sum_{n'=1}^{N-2} a_n^{\mu\nu} b_j^{(N-3)} R_n^{\mu\nu} \right] \right) dr_i dr_j.
\tag{2.60}
\]

The last integral after some algebraic manipulation becomes

\[
\langle \omega_\mu(r_i, r_j) | \frac{1}{|r_i - r_j|} | \omega_\nu(r_i, r_j) \rangle = \exp \left[ -a_i^{\mu\nu} (R_i^{\mu\nu})^2 - a_j^{\mu\nu} (R_j^{\mu\nu})^2 \right] \times
\exp \left[ [(a_i^{\mu\nu} R_i^{\mu\nu} - Y_i^{\mu\nu}), (a_j^{\mu\nu} R_j^{\mu\nu} - Y_j^{\mu\nu})] \right] \times
\left( \begin{array}{cc}
D'(i) & -b_i^{(N-2)} \\
-b_{ij}^{(N-2)} & D'(j)
\end{array} \right) \left[ (a_i^{\mu\nu} R_i^{\mu\nu} - Y_i^{\mu\nu}), (a_j^{\mu\nu} R_j^{\mu\nu} - Y_j^{\mu\nu}) \right] \right) \times
\langle \tilde{\omega}_\mu(r_i, r_j) | \frac{1}{|r_i - r_j|} | \tilde{\omega}_\nu(r_i, r_j) \rangle,
\tag{2.61}
\]

and

\[
\langle \tilde{\omega}_\mu(r_i, r_j) | \frac{1}{|r_i - r_j|} | \tilde{\omega}_\nu(r_i, r_j) \rangle = \int \int \exp \left[ -D'(i) \left| r_i - D'(i)^{-1} (a_i^{\mu\nu} R_i^{\mu\nu} - Y_i^{\mu\nu} - b_{ij}^{(N-2)} r_j)^2 \right|^2 \right] \frac{1}{|r_i - r_j|} \times
\]
\[
\exp \left[ -\frac{D'(i,j)}{D'(i)} \right] r_j - D'(i,j)^{-1} [D'(i)(a_i^{\mu\nu} R_j^{\mu\nu} - Y_j^{\mu\nu})
- b_j^{(N-2)}(a_i^{\mu\nu} R_i^{\mu\nu} - Y_i^{\mu\nu})] \right] dr_i dr_j,
\]

where

\[
D'(i) = a_i^{\mu\nu} + b_i^{(N-2)}, \quad D'(j) = a_j^{\mu\nu} + b_j^{(N-2)},
\]

\[
D'(i,j) = \begin{vmatrix}
    a_i^{\mu\nu} + b_i^{(N-2)} & b_i^{(N-2)} \\
    b_j^{(N-2)} & a_j^{(N-2)} + b_j^{(N-2)}
\end{vmatrix}
\]

(2.62)

and

\[
Y_i^{\mu\nu} = \frac{1}{\det(A^{\mu\nu} + B^{\mu\nu}; i, j)} \sum_{n=1}^{N-2} a_n^{\mu\nu} \tilde{b}^{(N-3)} R_n^{\mu\nu};
\]

\[
Y_j^{\mu\nu} = \frac{1}{\det(A^{\mu\nu} + B^{\mu\nu}; i, j)} \sum_{n'=1}^{N-2} a_{n'}^{\mu\nu} \tilde{b}^{(N-3)} R_{n'}^{\mu\nu}.
\]

(2.64)

In order to evaluate the two-electron integral we replace each quantity in the integrand by its Fourier transform

\[
\langle \tilde{\omega}_\mu(r_i, r_j) | \frac{1}{|r_i - r_j|} | \tilde{\omega}_\nu(r_i, r_j) \rangle = 4\pi \frac{1}{(2\pi)^5} \times
\]

\[
\left( \frac{\pi^2}{D'(i,j)} \right)^{\frac{3}{2}} \iiint dr_i dr_j dk_1 dk_2 dk_3 \exp \left( -\frac{k_1^2}{4D'(i)} \right) \exp \left( -\frac{k_3^2}{4D'(i,j)} \right) \times
\]

\[
k_2^{-2} \exp[ik_1 \cdot (r_i - D'(i)^{-1}[a_i^{lk} R_i^{lk} - Y_i^{lk}] - b_i^{(N-2)} r_j)] \exp[ik_2 \cdot (r_i - r_j)] \times
\]

\[
\exp \left[ ik_3 \cdot (r_j - D'(i,j)^{-1} \times
\]

\[
[D'(i)(a_i^{lk} R_j^{lk} - Y_j^{lk}) - b_i^{(N-2)}(a_i^{lklk} R_i^{lk} - Y_i^{lk})] \right].
\]
\[= 4\pi (2\pi)^{-3} \left( \frac{\pi^2}{D'(i,j)} \right)^{\frac{3}{2}} \iiint dk_1 dk_2 dk_3 \exp \left( \frac{-k_1^2}{4D'(i,j)} \right) \exp \left( \frac{-k_2^2}{4D'(i,j)} \right) \times k_2^{-2} \exp[-iD'(i,j)^{-1}k_3 \cdot [D'(i)(a_{\mu\nu}^\tau \mathbf{R}_j^\tau - Y_j^\mu)] \exp[-iD'(i)^{-1}k_1 \cdot (a_{\mu\nu}^\tau \mathbf{R}_i^\mu - Y_i^\nu)] \times \delta(k_1 + k_2) \delta(k_3 - k_2 + D'(i)^{-1}b_{ij}^{(N-2)} k_1). \]

Setting \(k_1 = -k_2\) and \(k_3 = [1 + D'(i)^{-1}b_{ij}^{(N-2)}]k_2\) and relabeling \(k_2\) as \(k\) one obtains

\[\langle \bar{\omega}_\mu(r_i, r_j)| \frac{1}{|r_i - r_j|} | \bar{\omega}_\nu(r_i, r_j) \rangle = \]

\[\frac{1}{2\pi^2} \left( \frac{\pi^2}{D'(i,j)} \right)^{\frac{3}{2}} \int dk k_2^{-2} \exp \left[ \frac{-k_2^2(D'(i) + D'(j) + 2b_{ij}^{(N-2)})}{4D'(i,j)} \right] \times \exp \left[ ik \cdot \left( \frac{D'(i) + 2b_{ij}^{(N-2)}}{D'(i,j)} \right) (a_{\mu\nu}^\tau \mathbf{R}_i^\mu - Y_i^\nu) \right.\]

\[\left. - \left( \frac{D'(j) + 2b_{ij}^{(N-2)}}{D'(i,j)} \right) (a_{\mu\nu}^\tau \mathbf{R}_j^\mu - Y_j^\nu) \right]. \]

By introducing the error function, the final formula for the electron repulsion integral becomes

\[\langle \omega_\mu(r_1, r_2, ..., r_N)| \frac{1}{|r_i - r_j|} | \omega_\nu(r_1, r_2, ..., r_N) \rangle = \]

\[\pi^{3(N-2)} K_{kl}[\text{det}(A^\mu^\nu + B^\mu^\nu; i,j)]^{-\frac{3}{2}} \exp \left[ -\frac{1}{\text{det}(A^\mu^\nu + B^\mu^\nu; i,j)} \times \right.\]

\[(\mathbf{R}_1^\mu, ..., \mathbf{R}_N^\mu; i,j)S(1, ..., N; i,j)(\mathbf{R}_1^\nu, ..., \mathbf{R}_N^\nu; i,j)^T \times \]

\[\exp \left( [a_{i\mu\nu}^\tau \mathbf{R}_i^\mu - Y_i^\nu], (a_{j\mu\nu}^\tau \mathbf{R}_j^\mu - Y_j^\nu)] \times \right.\]

\[\left. \left( \begin{array}{cc} D'(i) & -b_{ij}^{(N-2)} \\ -b_{ij}^{(N-2)} & D'(j) \end{array} \right) \left( \begin{array}{cc} a_{i\mu\nu}^\tau \mathbf{R}_i^\mu - Y_i^\nu \\ a_{j\mu\nu}^\tau \mathbf{R}_j^\mu - Y_j^\nu \end{array} \right) \right] \times \]

\[\exp \left[ -a_{i\mu\nu}^\tau (\mathbf{R}_i^\mu)^2 - a_{j\mu\nu}^\tau (\mathbf{R}_j^\mu)^2 \right] \frac{2\pi^{\frac{5}{2}}}{D'(i,j)[D'(i) + D'(j) + 2b_{ij}^{(N-2)}]^{\frac{5}{2}}} \times \]
For the completion of the discussion, we will now demonstrate the evaluation of the kinetic energy integral. This integral may be expressed as an appropriate combination of generalized overlap integrals. In order to demonstrate this we integrate the kinetic energy integral by parts which leads to the following integral

\[ I_i^{\mu\nu} = \int \ldots \int [\nabla_i \omega_\mu (r_1, r_2 \ldots r_N)] [\nabla_i \omega_\nu (r_1, r_2 \ldots r_N)] dr_1 dr_2 \ldots dr_N. \]  

(2.69)

Substituting the expression for \( \omega_\mu \) and \( \omega_\nu \) into the above integral and performing differentiation with respect to the coordinates of the \( i \)-th particle we get

\[ I_i^{\mu\nu} = 4 K_{\mu\nu} \int \ldots \int \left[ \alpha_i^\mu (r_i - R_i^\mu) + \sum_{m=1}^{N} b_{im}^\mu r_m \right] \left[ \alpha_i^\nu (r_i - R_i^\nu) + \sum_{s=1}^{N} b_{is}^\nu r_s \right] \times \]

\[ \exp \left( -\sum_{n=1}^{N} a_n^{\mu\nu} |r_n - R_n^{\mu\nu}|^2 - r B^{\mu\nu} r^T \right) dr_1 dr_2 \ldots dr_N \]  

(2.70)

Before we expand the last integral, let us define the generalized overlap integral

\[ J(r_p, r_q; n_1, n_2) = \]

\[ \int \ldots \int r_p^{n_1} r_q^{n_2} \exp \left( -\sum_{n=1}^{N} a_n^{\mu\nu} |r_n - R_n^{\mu\nu}|^2 - r B^{\mu\nu} r^T \right) dr_1 dr_2 \ldots dr_N \]  

(2.71)

Using the above integral, the kinetic energy integral becomes

\[ I_i^{\mu\nu} = 4 K_{\mu\nu} \left[ \alpha_i^\mu \alpha_i^\nu J(r_i, r_i; 1, 1) - \alpha_i^\mu \alpha_i^\nu (R_i^\mu + R_i^\nu) J(r_i, r_i; 1, 0) \right. \]

\[ + \alpha_i^\mu \alpha_i^\nu R_i^\mu R_i^\nu J(r_i, r_i; 0, 0) + \alpha_i^\mu \sum_{s=1}^{N} b_{is}^\nu J(r_i, r_s; 1, 1) + \alpha_i^\nu \sum_{m=1}^{N} b_{im}^\mu J(r_i, r_m; 1, 1) \]

\[ \left. - \alpha_i^\mu R_i^\mu \sum_{s=1}^{N} b_{is}^\nu J(r_i, r_s; 0, 1) - \alpha_i^\nu R_i^\nu \sum_{m=1}^{N} b_{im}^\mu J(r_i, r_m; 0, 1) \right] \]
The kinetic energy integral contains combinations of three types of the generalized overlap integrals $J(r_p, r_q; n_1, n_2)$. The integral with $n_1 = n_2 = 0$ is the overlap integral already discussed. The integrals with $n_1 = n_2 = 1$ can be calculated as a partial derivative of the overlap integral with respect to the nonlinear correlation parameter $b^\mu\nu_{pq}$,

$$
J(r_p, r_q; 1, 1) = \frac{-1}{2 - \delta_{pq}} \frac{\partial}{\partial b^\mu\nu_{pq}} \langle \omega_\mu | \omega_\nu \rangle,
$$

(2.73)

where $\delta_{sm}$ is the Kronecker delta. The last type of integral with $n_1 = 0$ and $n_2 = 1$ can be calculate as a partial derivative of the overlap integral with respect to the orbital parameter $a^\mu_\nu$,

$$
\int \ldots \int |r_p - R^\mu_\nu|^2 \exp \left[ -\sum_{n=1}^{N} a^\mu_\nu |r_n - R^\mu_\mu|^2 - rB^\mu_\nu r^T \right] dr_1 \ldots dr_N.
$$

(2.74)

After some algebraic manipulations the last expression becomes

$$
- \frac{\partial}{\partial a^\mu_\nu} \langle \omega_\mu | \omega_\nu \rangle = - \frac{\partial}{\partial b^\mu_\nu} \langle \omega_\mu | \omega_\nu \rangle - 2R^\mu_\nu J(r_p, r_q; 1, 0) + (R^\mu_\nu)^2 \langle \omega_\mu | \omega_\nu \rangle.
$$

(2.75)

Finally, one obtains the following expression for the $J(r_p, r_q; 1, 0)$ integral

$$
J(r_p, r_q; 1, 0) = - \frac{1}{2} \left( R^\mu_\nu \right)^{-1} \left[ \frac{\partial}{\partial a^\mu_\nu} \langle \omega_\mu | \omega_\nu \rangle - \frac{\partial}{\partial b^\mu_\nu} \langle \omega_\mu | \omega_\nu \rangle \right] + \frac{1}{2} R^\mu_\nu \langle \omega_\mu | \omega_\nu \rangle.
$$

(2.76)

The kinetic energy integral for the CM motion can evaluated in very similar way. In Appendix C the evaluation is demonstrated for the $H^+_2$ molecule. All of the presented integrals in this section have compact forms similar to the integrals for the Gaussian orbitals. The reduction procedure allows us to represent all integrals in terms of the elementary integrals. From the computational point of view this strategy facilitates an effective scheme for the practical implementation.
2.5 MANY-BODY WAVE FUNCTION WITH HIGHER ANGULAR MOMENTUM

In the previous section we presented evaluation of multi-center and multi-particle integrals for the s-type explicitly correlated Gaussian-type functions (called the cluster functions). The angular dependence of Gaussian functions can be achieved explicitly through the use of spherical harmonics, or equivalently through the use of integer powers of the appropriate Cartesian coordinates. In order to generate a cluster function with higher angular momenta one multiplies the s-type cluster by an appropriate power of the coordinates of the particle positions with respect to the orbital centers

\[ \phi_p(\{l_p^\mu, m_p^\mu, n_p^\mu\}, \{r_p\}, \{R_p^\mu\}, \{a_p^\mu\}, \{b_p^\mu\}) = \prod_{p=1}^{N} \left[ (x_p - R_{p,x}^\mu)^l_p^\mu (y_p - R_{p,y}^\mu)^m_p^\mu (z_p - R_{p,z}^\mu)^n_p^\mu \right] \omega_\mu, \quad (2.77) \]

where \(\{l_p^\mu, m_p^\mu, n_p^\mu\}\) will be called the "angular momentum" of the Gaussian cluster function, exactly the same as for the orbital Gaussians. The next step in our consideration is to determined multi-particle and multi-center integrals involving Gaussian cluster functions and the components of the nonrelativistic Hamiltonian. This task may be accomplished in two different ways. The first procedure is based on the application of the Fourier transform and the convolution theorem as originally presented by Lester and Kraus [53]. However, an extension of this procedure for functions which involve more than two particles becomes quite complicated and difficult in a practical realization. The second procedure to obtain these integrals comes from Boys classic paper [50]. This procedure is based on the observation that a higher angular momentum function can be generated by successive differentiations of the s-type Gaussian function with respect to the coordinates of the orbital centers. Because we already demonstrated the evaluation of the integrals with s-type cluster functions, one can now generalize our algorithms for the Cartesian cluster functions using Boys procedure. This involves expressing the functions with higher angular
momenta in terms of the raising operators

\[
\phi_\mu(l^\mu_i, m^\mu_i, n^\mu_i), \{r_p\}, \{R^\mu_p\}, \{a^\mu_p\}, \{b^\mu_p\}) = \prod_{p=1}^{N} \left[ \hat{M}_{x}^{\mu_p} \hat{M}_{y}^{\mu_p} \hat{M}_{z}^{\mu_p} \right] \omega_\mu,
\]

(2.78).

The raising operator, \( \hat{M}^n \), is expressed as a series of partial derivatives with respect to the coordinates of the orbital centers

\[
\hat{M}^n_z = \sum_{m=0}^{[n/2]} C_n^m \frac{\partial^{n-2m}}{\partial R^2_{z,2m}}.
\]

(2.79)

where

\[
C_n^m = \frac{n!}{2^n \alpha^{n-m} m! (n-2m)!}.
\]

(2.80)

This form of the raising operators has been recently used by Schlegel [77,78] for computing second derivatives of two electron integrals over s and p Cartesian orbital Gaussians. Using the above definition we may generate any angular functions from \( \omega_\mu \) as is outlined in the next section.

Let us now summarize some properties of the Gaussian functions. First, a product of two s-Gaussian functions is a Gaussian function times a factor

\[
\omega_\mu \omega_\nu = K_{\mu\nu} \omega_{\mu\nu},
\]

(2.81)

where

\[
\omega_{\mu\nu} = \exp \left(- \sum_{i=1}^{N} a^\mu_i |r_i - R^\mu_i|^2 - rB^\mu_i r^T \right),
\]

(2.82)

with

\[
R^\mu_i = \frac{\alpha^\mu_i R^\mu_i + \alpha^\nu_i R^\nu_i}{\alpha^\mu_i + \alpha^\nu_i}; \quad a^\mu_i = \alpha^\mu_i + \alpha^\nu_i; \quad B^\mu = B^\mu + B^\nu,
\]

(2.83)

and \( K_{\mu\nu} \) is equal to

\[
K_{\mu\nu} = \exp \left(- \sum_{i=1}^{N} \frac{\alpha^\mu_i \alpha^\nu_i}{\alpha^\mu_i + \alpha^\nu_i} |r_i - R^\nu_i|^2 \right).
\]

(2.84)

Using these properties for the Gaussian with higher angular momenta the above relation becomes \((x_p - R^\mu_{p,x}) \equiv x_p, R^\mu_{p,x}\)

\[
\prod_{p=1}^{N} \left[ \left( x_p^{m^\mu_p} y_p^{m^\mu_p} z_p^{m^\mu_p} \right) \left( y_p^{m^\mu_p} z_p^{m^\mu_p} x_p^{m^\mu_p} \right) \left( z_p^{m^\mu_p} x_p^{m^\mu_p} y_p^{m^\mu_p} \right) \right] \omega_\mu \omega_\nu =
\]
By expanding the polynomial of coordinates and center positions with respect to the common centers one gets

\[ K_{\mu \nu} \prod_{p=1}^{N} \left[ \left( x_{p,R_{p,x}}^{l_{pR_{p,x}}^l} \right) \left( y_{p,R_{p,y}}^{m_{pR_{p,y}}^m} \right) \left( z_{p,R_{p,z}}^{n_{pR_{p,z}}^n} \right) \right] \omega_{\mu \nu}. \]  

(2.85)

The Eq.(2.85) takes the form (for simplicity only \( x \)-component is shown)

\[ \sum_{\lambda} f_{\lambda,\mu} \left( l_{p}^{l_{p}} R_{p,x} \right) x_{p,R_{p}}^{\lambda} = \sum_{\lambda} f_{\lambda,\mu} \left( l_{p}^{l_{p}} R_{p,x} \right) x_{p,R_{p}}^{\lambda} \]

(2.86)

with

\[ f_{j}(l,m,a,b) = \sum_{i=(0,j-m)}^{(j,b)} \binom{l}{i} \binom{m}{j-i} a^{l-i} b^{m+i-j}, \]

(2.87)

and

\[ R_{p,x}^{\mu \nu} = R_{p,x}^{\mu \nu} - R_{p,x}^{\mu \nu}. \]

(2.88)

The properties and the notation outlined in this section will be used in the next section to evaluate the multiparticle integrals.

## 2.6 Generating Scheme for Molecular Integrals

Let us consider the following general molecular integral

\[ O_{\mu \nu} = \int \int \ldots \int \phi_{\mu} \Phi_{\nu} \prod_{q=1}^{N} dx_{q}, \]

(2.90)

If the operator \( \hat{O} \) commutes with the Gaussian function the integral can be rewritten as follows

\[ O_{\mu \nu} = K_{\mu \nu} \int \int \ldots \int \Phi_{\mu} \prod_{p=1}^{N} dx_{p}, \]

(2.91)

and according to the previous section becomes

\[ O_{\mu \nu} = K_{\mu \nu} \prod_{p=1}^{N} \left[ M_{x}^{l_{pR_{p,x}}^l} M_{y}^{m_{pR_{p,y}}^m} M_{z}^{n_{pR_{p,z}}^n} \right] \int \int \ldots \int \Phi_{\mu \nu} \prod_{p=1}^{N} dx_{p}. \]

(2.92)
The last expression contains only integrals with the spherical functions. Using the above scheme we can now evaluate the overlap integral, the nuclear attraction integral and the electron repulsion integral. The procedure cannot be applied to the kinetic energy integral. However, this integral can be expressed as a linear combination of the overlap integrals as it will be shown later.

2.7 MOLECULAR INTEGRALS OVER CARTESIAN GAUSSIANS

First, let us consider the general overlap integral (OV) which can be written as a product of three components

$$\int \ldots \int \phi_\mu \phi_\nu \prod_{p=1}^{N} dx_p = K_{\mu \nu} I_x I_y I_z. \quad (2.93)$$

Each of the components has the same form. For example the $x$-term is equal to

$$I_x = \prod_{j=1}^{N} \sum_{i_j}^{l_{ij}^x+l_{ij}^x} f_{ij,x}(l_{ij}^x, l_{ij}^x, R_{j,x}^\mu R_{j,x}^\nu R_{j,x}^\mu, R_{j,x}^\nu R_{j,x}^\mu) \times$$

$$\int \ldots \int x_{j,x} R_{j,x}^\mu \omega_{\mu \nu,x} \prod_{p=1}^{N} dx_p. \quad (2.94)$$

In terms of the raising operator the last integral can be expressed as follows

$$I_x = \prod_{j=1}^{N} \sum_{i_j}^{l_{ij}^x+l_{ij}^x} f_{ij,x}(l_{ij}^x, l_{ij}^x, R_{j,x}^\mu R_{j,x}^\nu R_{j,x}^\mu, R_{j,x}^\nu R_{j,x}^\mu) \times$$

$$\tilde{M}_{ij}^{x} \int \ldots \int \omega_{\mu \nu,x} \prod_{p=1}^{N} dx_p. \quad (2.95)$$

Combining the above result with the one-dimensional equivalent of Eq.(2.54) one obtains

$$I_x = \pi \frac{N}{2} [det(A^\mu^\nu + B^\mu^\nu)]^{-\frac{1}{2}} \times$$
\[
\sum_{j=1}^{N} \prod_{i} \sum_{i} \sum_{r} f_{ij,x} \left( l^{i}_{j}, l^{i}_{j}, R^{i}_{j,x} R^{i}_{j,x}, R^{i}_{j,x} R^{i}_{j,x} \right) C_{ij}^{l} \frac{\partial^{2r_{j}}}{\partial \left( R^{i}_{j,x} \right)^{2r_{j}}} \times \\
\exp \left[ -\frac{1}{\text{det}(A^{\mu\nu} + B^{\mu\nu})} \left( R^{\mu\nu}_{1,x}, \ldots, R^{\mu\nu}_{N,x} \right) S(1, \ldots, N) \left( R^{\mu\nu}_{1,x}, \ldots, R^{\mu\nu}_{N,x} \right)^{T} \right],
\]

(2.96)

where the definition of \( C_{ij}^{l} \) has been introduced in the previous section. One could derive the final form of the above equation by a direct differentiation with respect to the coordinates of the orbital centers. However, instead of doing this directly, we use a less cluttered procedure based on a unitary transformation of the quadratic form appearing in the exponent. This procedure should be also more efficient from the computational point of view. Let us introduce the unitary matrix \( U \) which diagonalizes the matrix \( S(1,2,\ldots,N) \),

\[
(R^{\mu\nu}_{1,x}, \ldots, R^{\mu\nu}_{N,x}) U U^{T} S(1, \ldots, N) U U^{T} (R^{\mu\nu}_{1,x}, \ldots, R^{\mu\nu}_{N,x})^{T} = \\
\sum_{m=1}^{N} \tilde{S}_{mm}(\tilde{R}^{\mu\nu}_{m,x})^{2}.
\]

(2.97)

By introducing the above transformation into Eq.(2.96), the overlap integral \( I_{x} \) becomes

\[
I_{x} = \pi \frac{N}{2} \left[ \text{det}(A^{\mu\nu} + B^{\mu\nu}) \right]^{-\frac{1}{2}} \times \\
\prod_{j=1}^{N} \prod_{i} \sum_{r} f_{ij,x} \left( l^{i}_{j}, l^{i}_{j}, R^{i}_{j,x} R^{i}_{j,x}, R^{i}_{j,x} R^{i}_{j,x} \right) C_{ij}^{l} \times \\
\left( \sum_{k} U_{kj} \frac{\partial}{\partial \tilde{R}^{\mu\nu}_{k,j,x}} \right)^{l} \frac{\partial^{2r_{j}}}{\partial \left( \tilde{R}^{\mu\nu}_{k,j,x} \right)^{2r_{j}}} \exp \left[ -\frac{\tilde{S}_{jj}(\tilde{R}^{\mu\nu}_{j,x})^{2}}{\text{det}(A^{\mu\nu} + B^{\mu\nu})} \right].
\]

(2.98)

By performing differentiation with respect to the coordinates of the orbital centers, the last equation can be rewritten in the following way

\[
\prod_{j=1}^{N} \left( \sum_{k} U_{kj} \frac{\partial}{\partial \tilde{R}^{\mu\nu}_{k,j,x}} \right)^{l} \frac{\partial^{2r_{j}}}{\partial \left( \tilde{R}^{\mu\nu}_{k,j,x} \right)^{2}} = \\
\sum_{m_{1}+m_{2}+\ldots+m_{N}=n} \prod_{j=1}^{N} \left( \frac{g_{ij}^{m_{j}}}{m_{j}!} \frac{\partial^{m_{j}}}{\partial \left( \tilde{R}^{\mu\nu}_{j,x} \right)^{m_{j}}} \right),
\]

(2.99)

where the coefficient \( g_{ij}^{m_{j}} \) results from the expansion, and the summation occurs for \( n = \sum_{j=1}^{N} (i_{j} - 2r_{j}) \). In order to evaluate the derivative in Eq.(2.98), one can use
the properties of the Hermite polynomials

\[ H_n(z) = (-1)^n \exp(z^2) \frac{d^n}{dz^n} \exp(-z^2) = u! \sum_{n=0}^{[u/2]} \frac{(-1)^n (2z)^{u-2n}}{n! (u-2n)!}. \] (2.100)

After some manipulations we get

\[ \frac{\partial^{m_j}}{\partial (\tilde{R}_{j,x}^{\mu\nu})^{m_j}} \exp \left[ -\frac{\tilde{S}_{jj}}{\det(A^{\mu\nu} + B^{\mu\nu})} (\tilde{R}_{j,x}^{\mu\nu})^2 \right] = \]

\[ (-1)^{m_j} \left[ \frac{\tilde{S}_{jj}}{\det(A^{\mu\nu} + B^{\mu\nu})} \right]^{\frac{1}{2}(m_j)} \times \]

\[ \exp \left[ -\frac{\tilde{S}_{jj}}{\det(A^{\mu\nu} + B^{\mu\nu})} (\tilde{R}_{j,x}^{\mu\nu})^2 \right] H_{m_j} \left( \left[ \frac{\tilde{S}_{jj}}{\det(A^{\mu\nu} + B^{\mu\nu})} \right]^{\frac{1}{2}} \tilde{R}_{j,x}^{\mu\nu} \right). \] (2.101)

The one-dimensional overlap integral is equal to

\[ I_x = \pi^{K/2} \left[ \det(A^{\mu\nu} + B^{\mu\nu}) \right]^{-\frac{1}{2}} \times \]

\[ \exp \left[ -\frac{1}{\det(A^{\mu\nu} + B^{\mu\nu})} (R_{1,x}^{\mu\nu}, \ldots, R_{N,x}^{\mu\nu}) S(1, \ldots, N)(R_{1,x}^{\mu\nu}, \ldots, R_{N,x}^{\mu\nu})^T \right] \times \]

\[ \prod_{j=1}^{N} \sum_{i} \sum_{r} (-1)^{i_j} f_{i_j,x} (l_{i,j}^{\mu\nu}, R_{j,x}^{\mu\nu}) \times \]

\[ C_{i_j}^{i_{j-2r_j}} \left[ \frac{1}{\det(A^{\mu\nu} + B^{\mu\nu})} \right]^{\frac{1}{2}(i_j-2r_j)} \times \]

\[ \sum_{m_1 + m_2 + \ldots + m_N = n} \prod_{k=1}^{N} \left[ \frac{g_{k}^{m_k}}{m_k!} \tilde{S}_{kk}^{m_k} H_{m_k} \left( \left[ \frac{\tilde{S}_{kk}}{\det(A^{\mu\nu} + B^{\mu\nu})} \right]^{\frac{1}{2}} \tilde{R}_{k,x}^{\mu\nu} \right) \right]. \] (2.102)

The form of the last equation allows us to apply the summation theorem for the Hermite polynomials

\[ \sum_{m_1 + m_2 + \ldots + m_N = n} \prod_{k=1}^{N} \left[ \frac{g_{k}^{m_k}}{m_k!} \tilde{S}_{kk}^{m_k} H_{m_k} \left( \left[ \frac{\tilde{S}_{kk}}{\det(A^{\mu\nu} + B^{\mu\nu})} \right]^{\frac{1}{2}} \tilde{R}_{k,x}^{\mu\nu} \right) \right] = \]
Finally, the three-dimensional overlap matrix reads

\[
\frac{1}{n!} \left( \sum_{k=1}^{N} \tilde{S}_{kkg_2^{m_k}} \right)^{\frac{1}{n}} H_n \left( \frac{\sum_{k=1}^{N} \tilde{S}_{kkg_2^{m_k}} \tilde{R}_{k,\nu}^{\mu}}{\text{det}(A^\mu + B^\nu)} \sqrt{\sum_{k=1}^{N} \tilde{S}_{kkg_2^{2m_k}}} \right).
\]  

(2.103)

Finally, the three-dimensional overlap matrix reads

\[
OV = \pi^{\frac{3N}{2}} K_{\mu\nu}[\text{det}(A^\mu + B^\nu)]^{-\frac{3}{2}} \times
\exp \left[ -\frac{1}{\text{det}(A^\mu + B^\nu)} \left( R_1^\mu, \ldots, R_N^\mu \right) S(1, \ldots, N)(R_1^\mu, \ldots, R_N^\mu)^T \right] \times
\prod_{j=1}^{N} \sum_{i_j, r_j, u} A_{i_j,r_j,u}^{(x)} \sum_{k_j,s_j,v} A_{k_j,s_j,v}^{(y)} \sum_{l_j,t_j,w} A_{l_j,t_j,w}^{(z)}
\]  

(2.104)

where \( A_{i_j,r_j,u}^{(x)} = \)

\[
(-1)^{i_j+u} f_{i_j,x}(l_j^\mu, l_j^\nu, R_{j,x}^\mu R_{j,x}^\nu, \tilde{R}_{j,x}^{\mu\nu} R_{j,x}^\nu) C_{i_j,r_j}^{ij} \left[ \frac{\sum_{k=1}^{N} \tilde{S}_{kkg_2^{2m_k}}}{\text{det}(A^\mu + B^\nu)} \right]^{\frac{1}{2}(i_j-2r_j)} \times
\]

\[
\left( \frac{\sum_{k=1}^{N} \tilde{S}_{kkg_2^{m_k}} \tilde{R}_{k,\nu}^{\mu}}{\text{det}(A^\mu + B^\nu)} \sqrt{\sum_{k=1}^{N} \tilde{S}_{kkg_2^{2m_k}}} \right) \left( \sum_{j=1}^{N} i_j - 2 \sum_{j=1}^{N} (r_j + u) \right) !
\]  

(2.105)

and the summation limit for \( u \) runs from zero to \([\frac{1}{2} \sum_{j=1}^{N} (i_j - 2r_j)]\). The last expression requires an additional comment: For the two particle case, we can determine the explicit form of the unitary transformation (2.97). Then one can easily show that the expression (2.105) becomes identical to the expression derived by Lester and Krauss [53]. For more than two particles the situation becomes more complicated and the diagonalization of the \( S(1, 2, \ldots, N) \) matrix has to be carried out numerically for each integral.

As we mentioned before, the kinetic energy integral can be expressed as a linear combination of the generalized overlap integrals. The integral can be split into three parts, i.e.

\[
\int \int \cdots \int \phi_{\mu} \left( \frac{1}{2} - \nabla_{p}^2 \right) \phi_{\nu} \prod_{s=1}^{N} d\tau_s =
\]
By noticing that
\[ \frac{1}{2} \frac{\partial^2}{\partial x_{p}^2} \phi_{\nu} = \left[ \frac{1}{2} l_{p}^{\nu} (l_{p}^{\nu} - 1) (x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu} - 2} - 2\alpha_{p}^{\nu} l_{p}^{\nu} (x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu} - 1} \right] \times \]
\[ \sum_{i=1}^{N} b_{i_p,x_i}^{\nu} (x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu} - 1} - (\alpha_{p}^{\nu} + b_{p,p}^{\nu}) (x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu}} + \]
\[ 2(\alpha_{p}^{\nu})^{2} l_{p}^{\nu} (x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu} + 2} \]
\[ + 4\alpha_{p}^{\nu} (x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu} + 1} (\sum_{i=1}^{N} b_{i_p,x_i}^{\nu}) + 2(x_{p} - R_{p,x}^{\nu})^{l_{p}^{\nu}} (\sum_{i=1}^{N} b_{i_p,x_i}^{\nu})^{2} \times \]
\[ \prod_{k=1}^{N} (y_{p} - R_{k,y}^{\nu})^{m_{p}^{\nu} (z_{p} - R_{p,z}^{\nu})^{n_{p}^{\nu}} \times \]
\[ \prod_{k=1}^{N} (x_{k} - R_{k,x}^{\nu})^{l_{k}^{\nu}} (y_{k} - R_{k,y}^{\nu})^{m_{k}^{\nu}} (z_{k} - R_{k,z}^{\nu})^{n_{k}^{\nu}} \omega_{\nu}, \]  
(2.107)

the kinetic energy integral can be treated as the sum of the overlap integrals.

Next, let us consider the Nuclear Attraction Integral (NA). First, by combining the Gaussian orbital factors to common centers the nuclear attraction integral becomes
\[
\int \cdots \int \frac{\phi_{\mu}}{|r_{p} - R_{c}|} \phi_{\nu} \prod_{s=1}^{N} dr_{s} = \]
\[
K_{\mu \nu} \prod_{j=1}^{N} l_{j}^{l_{j}^{\mu} + l_{j}^{\nu}} \sum_{i_{j}} f_{i_{j},x} (l_{j}^{\mu}, l_{j}^{\nu}, R_{j,x}^{\mu}, R_{j,x}^{\nu}) \times \]
\[
\sum_{i_{j}} f_{j, y} (m_{j}^{\mu}, m_{j}^{\nu}, R_{j,y}^{\mu}, R_{j,y}^{\nu}, R_{j,y}^{\mu}, R_{j,y}^{\nu}) \times \]
\[
\sum_{i_{j}} f_{i_{j}, x} (n_{j}^{\mu}, n_{j}^{\nu}, R_{j,z}^{\mu}, R_{j,z}^{\nu}, R_{j,z}^{\mu}, R_{j,z}^{\nu}) \times \]
\[
\int \cdots \int \frac{1}{|r_{p} - R_{c}|} R_{j,x}^{\mu} R_{j,x}^{\nu} \omega_{\mu \nu} \prod_{s=1}^{N} dx_{s}. \]  
(2.108)
Then introducing the raising operators, and with the use of the expression for spherical Gaussian integral, one obtains

\[ \text{NA} = \pi^{\frac{3(N-1)}{2}} K_{\mu\nu} \{ \text{det}(A^{\mu\nu} + B^{\mu\nu}; p) \}^{-\frac{3}{2}} \left( \frac{2\pi}{a_p^{\mu\nu} + b_p^{(N-1)}} \right) \times \]

\[ \prod_{j=1}^{N} \sum_{i_j} f_{i_j,x}(l_j^\mu, l_j^\nu, R_{j,x}^{\mu\nu} R_{j,x}^{\mu\nu}, R_{j,x}^{\mu\nu} R_{j,x}^{\mu\nu}) \times \]

\[ m_j^\mu + m_j^\nu \sum_{k_j} f_{k_j,y}(m_j^\mu, m_j^\nu, R_{j,y}^{\mu\nu} R_{j,y}^{\mu\nu}, R_{j,y}^{\mu\nu} R_{j,y}^{\mu\nu}) \times \]

\[ n_j^\mu + n_j^\nu \sum_{l_j} f_{l_j,x}(n_j^\mu, n_j^\nu, R_{j,z}^{\mu\nu} R_{j,z}^{\mu\nu}, R_{j,z}^{\mu\nu} R_{j,z}^{\mu\nu}) \times \]

\[ \hat{M}^{ij}_x \hat{M}^{kj}_y \hat{M}^{lj}_z \left[ \Lambda_1^{(x)} \Lambda_2^{(x)} \Lambda_1^{(y)} \Lambda_2^{(y)} \Lambda_1^{(z)} \Lambda_2^{(z)} F_0(t) \right], \quad (2.109) \]

where for simplification we used the following notation

\[ \Lambda_1^{(x)} = \exp \left[ \frac{1}{\text{det}(A^{\mu\nu} + B^{\mu\nu}, p)} \times \right. \]

\[ (R_{1,x}^{\mu\nu}, \ldots, R_{N,x}^{\mu\nu}; p)S(1, \ldots, N; p)(R_{1,x}^{\mu\nu}, \ldots, R_{N,x}^{\mu\nu}; p)^T \], \quad (2.110) \]

and

\[ \Lambda_2^{(x)} = \exp \left[ \frac{(a_p^{\mu\nu} R_{p,x}^{\mu\nu} - X_{p,x}^{\mu\nu})^2}{a_p^{\mu\nu} + b_p^{(N-1)}} - a_p^{\mu\nu} (R_{p,x}^{\mu\nu})^2 \right]. \quad (2.111) \]

In the next step let us consider the action of a product of raising operators on the \( \Lambda_1^{(x)} \Lambda_2^{(x)} F_0(W) \) quantities. After application of the Leibnitz formula one obtains

\[ \prod_{j=1}^{N} \hat{M}^{ij}_x \left[ \Lambda_1^{(x)} \hat{M}^{ij}_x \left( \Lambda_2^{(x)} F_0(W) \right) \right] = \prod_{j=1}^{N} \sum_{i_j} \sum_{j}\sum_{n_j} C_{i_j}^{[i_j/2]} (i_j - 2r_j) \times \]

\[ \left[ \frac{\partial^n \Lambda_1^{(x)}}{\partial (R_{ij,x}^{\mu\nu})^{n_j}} \right] \left[ \frac{\partial^{i_j-2r_j-n_j}}{\partial (R_{ij,x}^{\mu\nu})^{i_j-2r_j-n_j}} \hat{M}^{ij}_x \Lambda_2^{(x)} F_0(t) \right], \quad (2.112) \]
The partial derivative of $\Lambda_1^{(x)}$ with respect to the center position can be evaluated in the same way as for the general overlap integral. This involves determination of the unitary matrix $U(p)$, which diagonalizes the exponential quadratic form (without the $p$ coordinate), as follows:

$$
\prod_{j=1}^{N} \frac{\partial \Pi_{j \neq p}}{\partial (R_{j,x}^{\mu \nu})^{u_j}} \Lambda_1^{(x)} = \Lambda_1^{(x)} \prod_{j=1}^{N} \left[ \sum_{k \neq p}^{N} \frac{\tilde{S}_{jj}^{(p)} g_{k}^{2m_k}}{\det(A^{\mu \nu} + B^{\mu \nu}; p)} \right]^{\frac{1}{2}u_j} \times 
$$

$$
\times \left( \prod_{k=1}^{N} \sum_{k \neq p}^{N} \tilde{S}_{kk}^{(p)} g_{k}^{2m_k} \right)^{\frac{1}{2}u_p} \times 
$$

$$
H_{n_p} \left( \frac{\sum_{k=1}^{N} \tilde{S}_{kk}^{(p)} g_{k}^{2m_k}}{\det(A^{\mu \nu} + B^{\mu \nu}; p)} \right) . 
$$

(2.113) 

while the $\tilde{M}_x^{ip} \Lambda_2^{(x)} F_0(W)$ reads

$$
\tilde{M}_x^{ip} \Lambda_2^{(x)} F_0(W) = 
$$

$$
\sum_{r_p}^{[i_p/2]} \sum_{v_p}^{u_p} \sum_{u_p}^{r_p} \sum_{v_p}^{u_p} \sum_{v_p}^{u_p} C_{r_p}^{u_p} \left( \frac{i_p - 2r_p}{u_p} \right) \left[ \frac{u_p!}{(u_p - 2v_p)!} \right]^{i_p - 2r_p - u_p} \times 
$$

$$
\left[ \frac{2a_p^{\mu \nu}}{a_p^{\mu \nu} + b_p^{(N-1)}} \left( a_p^{\mu \nu} R_{p,x}^{\mu \nu} - X_{p,x}^{\mu \nu} \right) - 2a_p^{\mu \nu} R_{p,x}^{\mu \nu} \right] \times 
$$

$$
\left[ \frac{\partial i_p - 2r_p - u_p}{\partial (R_{p,x}^{\mu \nu})^{i_p - 2r_p - u_p}} F_0(t) \right] . 
$$

(2.114) 

Combining the above results, Eq.(2.111) can be rewritten in the following way

$$
\prod_{j=1}^{N} \tilde{M}_x^{ij} \left[ \Lambda_1^{(x)} \tilde{M}_x^{ij} \left( \Lambda_2^{(x)} F_0(W) \right) \right] = 
$$

$$
\Lambda_1^{(x)} \prod_{j=1}^{N} \sum_{i_j \neq p}^{[i_j/2]} \sum_{u_j}^{i_j - 2r_j} \sum_{u_j}^{i_j - 2r_j} C_{r_j}^{i_j} \left( \frac{i_j - 2r_j}{u_j} \right) \left[ \frac{\sum_{k \neq p}^{N} \tilde{S}_{jj}^{(p)} g_{k}^{2m_k}}{\det(A^{\mu \nu} + B^{\mu \nu}; p)} \right]^{\frac{1}{2}u_j} \times 
$$

$$
\times \left[ \sum_{k \neq p}^{N} \tilde{S}_{kk}^{(p)} g_{k}^{2m_k} \right]^{\frac{1}{2}u_p} \times 
$$

$$
H_{n_p} \left( \frac{\sum_{k \neq p}^{N} \tilde{S}_{kk}^{(p)} g_{k}^{2m_k}}{\det(A^{\mu \nu} + B^{\mu \nu}; p)} \right) . 
$$
The auxiliary function, \( F_m(t) \), has the following properties:

\[
F_m(t) = \int_0^1 u^{2m} \exp(-tu^2) du,
\]

and

\[
\frac{dF_m(t)}{dt} = -F_{m+1}(t).
\]

Performing differentiation with respect to \( R_{\mu\nu}^{(p)} \), one obtains

\[
\prod_{j=1}^{N} \frac{\partial \delta_{ij} - 2r_j - u_j}{\partial (R_{\mu\nu}^{(p)}_{j,x})_{ij} - 2r_j - u_j} \times
\]

\[
\left[ \Lambda_2^{(x)} \left[ X_{\mu\nu}^{(p,x)} + b_{pp}^{(N-1)} R_{\mu\nu}^{(p)} \right] u_p - 2v_p \frac{\partial \delta_{ij} - 2r_p - u_p}{\partial (R_{\mu\nu}^{(p)}_{j,x})_{ij} - 2r_p - u_p} F_0(t) \right] =
\]

\[
\sum_{w_p} (-1)^{w_p} \left( i_p - 2w_p - u_p \right) (2\alpha_{\mu\nu}^{(p)})_{i_p - 2r_p - u_p - 2w_p} \times
\]

\[
\left[ \frac{(\alpha_{\mu\nu}^{(p)})^2}{\alpha_{\mu\nu}^{(p)} + b_{pp}^{(N-1)}} \right]^{w_p} \frac{\partial \alpha_{\mu\nu}^{(p)} R_{\mu\nu}^{(p)}_{j,x}}{\partial (R_{\mu\nu}^{(p)}_{j,x})_{ij} - 2r_j - u_j} F_{w_p}(t).
\]

\[
\prod_{j=1}^{N} \frac{\partial \delta_{ij} - 2r_j - u_j}{\partial (R_{\mu\nu}^{(p)}_{j,x})_{ij} - 2r_j - u_j} \times
\]

\[
\left[ \Lambda_2^{(x)} \left[ X_{\mu\nu}^{(p,x)} + b_{pp}^{(N-1)} R_{\mu\nu}^{(p)} \right] u_p - 2v_p \frac{\partial \delta_{ij} - 2r_p - u_p}{\partial (R_{\mu\nu}^{(p)}_{j,x})_{ij} - 2r_p - u_p} F_0(t) \right].
\]
The final step contains evaluation of the last term in Eq.(2.118) which after transformation has the form

\[
\prod_{j=1}^{N} \frac{\partial^{i_j - 2r_j - u_j}}{\partial (R_{j,x}^{\mu \nu})^{i_j - 2r_j - u_j}} \left[ \Lambda_2^{(x)} \left[ X_{p,x}^{\mu \nu} + b_{pp}^{(N-1)} R_{p,x}^{\mu \nu} \right]^{u_p - 2v_p} F_w(t) \right] = \]

\[
\left[ \prod_{j=1}^{N} \left( \frac{a_{j,j}^{\mu \nu} b_{j,p}^{(N-2)}}{\det(A^{\mu \nu} + B^{\mu \nu})} \right) \right]^{i_j - 2r_j - u_j} \times \]

\[
\frac{\partial^{\eta_p}}{\partial (X_{p,x}^{\mu \nu})^{\eta_p}} \left[ \Lambda_2^{(x)} \left[ X_{p,x}^{\mu \nu} + b_{pp}^{(N-1)} R_{p,x}^{\mu \nu} \right]^{u_p - 2v_p} F_w(t) \right], \tag{2.119}
\]

where for simplification we used

\[
\eta_p = \sum_{j=1}^{N} (i_j - 2r_j - u_j). \tag{2.120}
\]

For the unrestricted sum in (2.120) we use:

\[
\eta = \sum_{j=1}^{N} (i_j - 2r_j - u_j). \tag{2.120a}
\]

Combining all the above results, the nuclear attraction integral can be expressed as follows

\[
NA = \pi^{3(N-1)/2} K_{\mu \nu} \det(A^{\mu \nu} + B^{\mu \nu})^{-3/2} \times \exp \left[ -\frac{1}{\det(A^{\mu \nu} + B^{\mu \nu})} \times \right.
\]

\[
(R_{1}^{\mu \nu}, \ldots, R_{N}^{\mu \nu}; p)S(1, \ldots, N; p)(R_{1}^{\mu \nu}, \ldots, R_{N}^{\mu \nu}; p)^T \times \]

\[
\left( \frac{2\pi}{a_{p}^{\mu \nu} + b_{pp}^{(N-1)}} \right) \exp \left[ \frac{(a_{p}^{\mu \nu} R_{p}^{\mu \nu} - X_{p}^{\mu \nu})^2}{a_{p}^{\mu \nu} + b_{pp}^{(N-1)}} - a_{p}^{\mu \nu} (R_{p}^{\mu \nu})^2 \right] \times \]

\[
\prod_{j=1}^{N} \sum_{j \neq p} B^{(x,p)}_{l_j, i_j, u_j} \sum_{k_j, s_j, v_j} B^{(y,p)}_{k_j, s_j, v_j} \sum_{l_j, t_j, w_j} B^{(z,p)}_{l_j, t_j, w_j} \times \]

\[
\sum_{i_p, r_p, u_p} \tilde{B}_{i_p, r_p, u_p} \sum_{i_p', r_p', u_p'} \tilde{B}_{i_p', r_p', u_p'} \sum_{i_p'', r_p'', u_p''} \tilde{B}_{i_p'', r_p'', u_p''} F_\sigma(t). \tag{2.122}
\]

where
\[
B_{i_j, r_j, u_j}^{(x, p)} = (-1)^{u_j} f_{i_j, x}(i_j^\mu, r_j^\mu, R_{j, x}^{\mu\nu}, R_{j, x}^{\mu\nu}, \frac{R_{j, x}^{\mu\nu}}{R_{j, x}^{\mu\nu}}) G_{r_j}^{i_j} \left(\frac{i_j - 2r_j}{u_j}\right) \frac{1}{(\sum_{k=1}^{N} 1_k)!} \times
\]
\[
\left(\frac{\alpha_j^{\mu\nu} \tilde{b}^{(N-2)}}{\text{det}(\mathcal{A}^{\mu\nu} + \mathcal{B}^{\mu\nu}; p)}\right)^{i_j - 2r_j - u_j} \times
\]
\[
\left[\frac{\sum_{k=1}^{N} \tilde{S}_{j k}^{(p)} g_{k}^{2m_k}}{\text{det}(\mathcal{A}^{\mu\nu} + \mathcal{B}^{\mu\nu}; p)}\right]^{\frac{1}{2} u_j} \cdot \left(\sum_{k=1}^{N} \tilde{S}_{j k}^{(p)} g_{k}^{2m_k}\right)^{\frac{1}{2} u_j} \times
\]
\[
H_{i_p} \left(\frac{\sum_{k=1}^{N} \tilde{S}_{j k}^{(p)} g_{k}^{2m_k} \tilde{R}_{j, x}^{\mu\nu}}{\sqrt{\sum_{k=1}^{N} \tilde{S}_{j k}^{(p)} g_{k}^{2m_x}}}, \right) \tag{4.30}
\]

and \(\tilde{B}_{i_p, r_p, u_p}\) has the form
\[
\tilde{B}_{i_p, r_p, u_p} = \left[\frac{u_p}{2}\right] \frac{[i_p - 2r_p - u_p]/2}{u_p} \frac{\eta_p}{\lambda_1/2} \frac{[\eta_p - \lambda_1 - \lambda_3]/2}{\lambda_3} \frac{(-1)^{w_p} C_{r_p}}{\alpha_p^{\mu\nu} + b^{(N-1)}_{pp}} \times
\]
\[
\eta_p! \frac{(i_p - 2r_p)!}{u_p!} \frac{(\eta_p - \lambda_1 - \lambda_3)!}{\lambda_3} \frac{(i_p - 2r_p - u_p - 2w_p)!}{\lambda_4} \times
\]
\[
\frac{2\alpha_p^{\mu\nu} u_p - 2w_p}{(\eta_p - \lambda_1)!} \frac{(\lambda_1 - 2\lambda_1)!}{(\eta - \lambda_1 - \lambda_3 - 2\lambda_4)!} \times
\]
\[
\left[\frac{-\alpha_p^{\mu\nu} b^{(N-1)}_{pp}}{\alpha_p^{\mu\nu} + b^{(N-1)}_{pp}}\right]^{u_p + \lambda_2} \frac{(-2\alpha_p^{\mu\nu})^{u_p - 2w_p + \lambda_1 - 2\lambda_2}}{(\alpha_p^{\mu\nu} + b^{(N-1)}_{pp})^{u_p - 2w_p + \lambda_1 - 2\lambda_2}} \times
\]
\[
\left[\frac{\alpha_p^{\mu\nu}}{\alpha_p^{\mu\nu} + b^{(N-1)}_{pp}}\right]^{w_p + \lambda_4} \frac{\left(\frac{\alpha_p^{\mu\nu} R_{p, x}^{\mu\nu}}{\alpha_p^{\mu\nu} + b^{(N-1)}_{pp}} - R_{c, x}^{\mu\nu}\right)^{\eta - 2w_p - \lambda_1 - \lambda_3 - 2\lambda_4}}{\left(\alpha_p^{\mu\nu} + b^{(N-1)}_{pp}\right)^{\eta - 2w_p - \lambda_1 - \lambda_3 - 2\lambda_4}} \times
\]
\[
\left[X_{p, x}^{\mu\nu} + b^{(N-1)}_{pp} R_{p, x}^{\mu\nu}\right]^{\lambda_1 - 2\lambda_2} W(\lambda_3). \tag{2.124}
\]
The $W(\lambda_3)$ in the last equation is equal to

$$W(\lambda_3) = \left( \frac{\eta_p - \lambda_1}{\lambda_3} \right) (u_p - 2v_p - \lambda_3)! \left[ X_{\mu,\nu,\rho}^{\mu,\nu,\rho} + b'_{\mu,\nu,\rho}^{(N-1)} R_{\mu,\nu,\rho}^{\mu,\nu,\rho} \right]^{u_p - 2v_p - \lambda_3},$$

(2.125)

when $u_p - 2v_p > \lambda_3$ and

$$W(\lambda_3) = (u_p - 2v_p)!,$$

(2.126)

when $u_p - 2v_p < \lambda_3$. Finally, $\sigma$ in Eq.(2.122) has three components

$$\sigma = \sigma_x + \sigma_y + \sigma_z,$$

(2.127)

with

$$\sigma_x = w_p + \eta_p - \lambda_1 - \lambda_3.$$

(2.128)

The last integral which is considered in this Chapter is the Electron Repulsion Integral (ER). The ER integral can be evaluated using the similar techniques applied previously to the OV and NA integrals. First, performing the contraction of orbital factors to common centers, one obtains

$$\int \cdots \int \phi_\mu \frac{1}{|r_p - r_q|} \phi_\nu \prod_{s=1}^{N} dr_s =$$

$$K_{\mu,\nu} \prod_{j=1}^{N} \sum_{i_j, k_j, l_j} f_{i_j,x}(l_{j,x}^{\mu}, l_{j,x}^{\nu}, R_{j,x}^{\mu}, R_{j,x}^{\nu}) \times$$

$$f_{k_j,y}(m_{j,y}^{\mu}, m_{j,y}^{\nu}, R_{j,y}^{\mu}, R_{j,y}^{\nu}, R_{j,y}^{\mu}, R_{j,y}^{\nu}) f_{i_j,x}(n_{j,x}^{\mu}, n_{j,x}^{\nu}, R_{j,x}^{\mu}, R_{j,x}^{\nu}, R_{j,x}^{\mu}, R_{j,x}^{\nu}) \times$$

$$\int \cdots \int \frac{1}{|r_p - r_q|} x^{i_j,R_{j}^{\mu}} y^{k_j,R_{j}^{\nu}} z^{l_j,R_{j}^{\mu}} \omega \prod_{s=1}^{N} dx_s.$$

(2.129)

Introducing the raising operators, and with the use of the expression for the spherical Gaussian integral, this integral can be written as follows:

$$\text{ER} = \pi^{\frac{3(N-2)}{2}} K_{\mu,\nu} [\det(A_{\mu,\nu} + B_{\mu,\nu}, p, q)]^{-\frac{3}{2}} \times$$

$$\frac{2\pi^{\frac{3}{2}}}{D'(p, q)[D'(p) + D'(q) + 2b'_{pq}^{(N-2)}]^{\frac{1}{2}}} \times$$
\[ \prod_{j=1}^{N} \sum_{i,j,k,l} f_{i,j,x}(R_{i,j,x}^{\mu}, R_{i,j,x}^{\nu}, R_{i,j,x}^{\rho}, R_{i,j,x}^{\sigma}) f_{l,y}(m_{j}^{\mu}, m_{j}^{\nu}, R_{j,y}^{\mu}, R_{j,y}^{\nu}, R_{j,y}^{\rho}, R_{j,y}^{\sigma}) \times \]
\[ f_{i,j,x}(n_{j}^{\mu}, n_{j}^{\nu}, R_{i,j,x}^{\mu}, R_{i,j,x}^{\nu}, R_{i,j,x}^{\rho}, R_{i,j,x}^{\sigma}) \times \]
\[ \hat{M}_{x}^{ij} \hat{M}_{y}^{kl} \hat{M}_{z}^{ij} \left[ \Xi_{1}(x) \Xi_{2}(y) \Xi_{1}(z) \Xi_{2}(Z) \right] F_{0}(Z) \] (2.130)

with
\[ \Xi_{1}(x) = \exp \left[ -\frac{1}{\det(A_{\mu \nu} + B_{\mu \nu}; p, q)} \times \right] \]
\[ (R_{1,\mu}, \ldots, R_{N,\mu}; p, q)S(1, \ldots, N; p, q)(R_{1,\mu}, \ldots, R_{N,\mu}; p, q)^{T}, \] (2.131)
\[ \Xi_{2}(x) = \exp \left[ -a_{p}^{\mu}\left(R_{p,x}^{\mu}\right)^{2} - a_{q}^{\mu}\left(R_{q,x}^{\mu}\right)^{2} \right] \times \]
\[ \exp \left( Q_{p,x}^{\mu}, Q_{p,x}^{\nu} \right) \left( \begin{array}{c} D'(p) \\ -b_{pq}^{(N-2)} \end{array} \right) \left[ Q_{p,x}^{\mu}, Q_{p,x}^{\nu} \right] \] (2.132)

and
\[ Z = \left[ \frac{D'(p) + 2b_{pq}^{(N-2)}}{D'(p, q)} \right] Q_{p,x}^{\mu} - \left[ \frac{D'(q) + 2b_{pq}^{(N-2)}}{D'(p, q)} \right] Q_{q,x}^{\mu} \right]^{2}. \] (2.133)

The raising operators for p and q particles can be explicitly separated in Eq.(2.130).

Application of the Leibnitz formula to the last term in Eq.(2.130) results in
\[ \prod_{j=1}^{N} \hat{M}_{x}^{ij} \left[ \Xi_{1}(x) \Xi_{2}(y) \Xi_{1}(z) \Xi_{2}(Z) \right] = \prod_{j=1}^{N} \left[ \frac{[i_{j}/2] i_{j} - 2r_{j}}{u_{j}} \right] \times \]
\[ \left[ \frac{\partial u_{j} \Xi_{1}(x)}{\partial (R_{i,j,x}^{\mu})^{u_{j}}} \right] \left[ \frac{\partial i_{j} - 2r_{j} - u_{j}}{\partial (R_{j,x}^{\mu})^{i_{j} - 2r_{j} - u_{j}}} \hat{M}_{x}^{i_{j}} \hat{M}_{x}^{i_{j}} \Xi_{2}(x) F_{0}(Z) \right]. \] (2.134)

The strategy of evaluation of the expression in the last square bracket is similar to the procedure discussed previously. Again, introducing the unitary matrix \( U(p,q) \) which diagonalizes the exponential quadratic form without p and q coordinates, the derivative becomes
\[ \prod_{j=1}^{N} \left[ \frac{\partial u_{j}}{\partial (R_{i,j,x}^{\mu})^{u_{j}}} \Xi_{1}(x) \right] \prod_{j=1}^{N} \left[ \frac{\sum_{k=1}^{N} \sum_{k \neq k} s_{k}^{(p,q)} g_{k}^{\mu_{2}m_{k}}}{\det(A_{\mu \nu} + B_{\mu \nu}; p, q)} \right]^{u_{j}} \times \]
The result of the action of the raising operators involving coordinates of particles \( p \) and \( q \) can be obtained as follows

\[
\mathcal{M}_L^{i_p} \mathcal{M}_L^{i_q} \left( \Xi^{(x)}_2 F_0(Z) \right) =
\]

\[
\Xi^{(x)}_2 \left( \sum_{r_p} \sum_{r_q} \sum_{u_p} \sum_{u_q} C_{r_p}^{i_p} C_{r_q}^{i_q} \left( \frac{i_p - 2r_p}{u_p} \right) \left( \frac{i_q - 2r_q}{u_q} \right) \right) \times
\]

\[
\left( \sqrt{\frac{1}{2} [D'(p)(a_p^{\mu\nu})^2 + a_p^{\mu\nu}]} \right)^{i_p - 2r_p} \left( \sqrt{\frac{1}{2} [D'(q)(a_q^{\mu\nu})^2 + a_q^{\mu\nu}]} \right)^{i_q - 2r_q} \times
\]

\[
\sum_{k=0}^{\min(i_p - 2r_p, i_q - 2r_q)} k! \left( \frac{i_p - 2r_p}{k} \right) \left( \frac{i_q - 2r_q}{k} \right) \times
\]

\[
\left( \frac{2b^{(N-2)}_p a_p^{\mu\nu} a_q^{\mu\nu}}{\sqrt{[D'(p)(a_p^{\mu\nu})^2 + a_p^{\mu\nu}][D'(q)(a_q^{\mu\nu})^2 + a_q^{\mu\nu}]}} \right)^k \times
\]

\[
H_{i_p - 2r_p - k} \left( \frac{b^{(N-2)} p a_p^{\mu\nu} Q^{\mu\nu} - D'(p)a_p^{\mu\nu} Q^{\mu\nu} - a_p^{\mu\nu} R_p^{\mu\nu}}{\sqrt{\frac{1}{2} [D'(p)(a_p^{\mu\nu})^2 + a_p^{\mu\nu}]}} \right) \times
\]

\[
H_{i_q - 2r_q - k} \left( \frac{b^{(N-2)} q a_q^{\mu\nu} Q^{\mu\nu} - D'(q)a_q^{\mu\nu} Q^{\mu\nu} - a_q^{\mu\nu} R_q^{\mu\nu}}{\sqrt{\frac{1}{2} [D'(q)(a_q^{\mu\nu})^2 + a_q^{\mu\nu}]}} \right) \times
\]

\[
\left[ \frac{\partial i_p - 2r_p - u_p}{\partial (R_p^{\mu\nu})_{i_p - 2r_p - u_p}} \frac{\partial i_q - 2r_q - u_q}{\partial (R_q^{\mu\nu})_{i_q - 2r_q - u_q}} F_0(Z) \right]. \quad (2.136)
\]

The next step in evaluation of the last equation contains differentiation of the \( F_0(Z) \) function. Let

\[
K_p = i_p - 2r_p - u_p, \quad (2.137)
\]

and

\[
K_q = i_q - 2r_q - u_q. \quad (2.138)
\]
and let us also assume for simplicity that $K_q > K_p$, then

$$
\left[ \frac{\partial_i \q^{2r_p - u_p}}{\partial (R_{p,x}^{\mu \nu})^{i-2r_p - u_p}} \frac{\partial_i \q^{2r_q - u_q}}{\partial (R_{q,x}^{\mu \nu})^{i-2r_q - u_q}} F_0 (Z) \right] =
$$

$$\sum_{w_1} \sum_{w_2} \sum_{w_3} \frac{(-1)^{w_1 + w_2} K_p! K_q! [(K_q - 2w_1 - K_p + w_2)]!}{w_1! w_3! (K_q - 2w_1)! (K_p - w_2)! (w_3 - 2w_2)!} \times
$$

$$\left[ \frac{(a_q^{\mu \nu})^2 [D'(p) + 2b_{pq}^{\mu \nu}(N-2)]}{D'(p) + D'(q) + 2b_{pq}^{\mu \nu}(N-2)} \right]^{w_1} \times
$$

$$\frac{-2a_p^{\mu \nu} a_q^{\mu \nu} [D'(p) + 2b_{pq}^{\mu \nu}(N-2)] [D'(q) + 2b_{pq}^{\mu \nu}(N-2)]}{[D'(p) + D'(q) + 2b_{pq}^{\mu \nu}(N-2)] D'(p, q)} \times K_p - w_3$$

$$\left[ \frac{(a_p^{\mu \nu})^2 [D'(q) + 2b_{pq}^{\mu \nu}(N-2)]}{D'(p) + D'(q) + 2b_{pq}^{\mu \nu}(N-2)} \right]^{w_3} \times
$$

$$\left( \frac{-2a_p^{\mu \nu} [D'(p) + 2b_{pq}^{\mu \nu}(N-2)]}{D'(p) + D'(q) + 2b_{pq}^{\mu \nu}(N-2)} \right)^{w_3} \times
$$

$$\left( \frac{2a_q^{\mu \nu} [D'(q) + 2b_{pq}^{\mu \nu}(N-2)]}{D'(p) + D'(q) + 2b_{pq}^{\mu \nu}(N-2)} \right)^{K_q - w_1 - K_p + w_2} \times
$$

$$\left( \frac{D'(p) + 2b_{pq}^{\mu \nu}(N-2)}{D'(p, q)} \right)^{2} Q_{p,x}^{\mu \nu} - \left( \frac{D'(q) + 2b_{pq}^{\mu \nu}(N-2)}{D'(p, q)} \right)^{K_q - K_p - 2w_1 + w_2 + w_3} \times F_{w_1 + w_2}(Z).$$

For the case when $K_q < K_p$ we have to simply exchange $q$ with $p$. In order to perform differentiation defined in Eq.(4.41), we express the derivative in terms of $\gamma_{p,x}^{\mu \nu}$ and $\gamma_{q,x}^{\mu \nu}$ Eq.(3.12)

$$\prod_{j=1}^{N} \frac{\partial_i \q^{2r_j - u_j}}{\partial (R_{j,x}^{\mu \nu})^{i-2r_j - u_j}} =
$$

$$\prod_{j=1}^{N} \frac{\alpha_j^{\mu \nu}}{dct(A_{\mu \nu}^{\nu} + B_{\mu \nu}^{\nu}; p, q)} \left[ \sum_{i_j} \times \right]
$$
\[
\left(i_j - 2r_j - u_j \right) \left(i_p (N-3)_{pq} \left( \delta_{qj} (N-3)_{ij} - 2r_{ij} - u_{ij} \right) \times \sum_{j=1}^{\eta_{pq}} \frac{\partial \eta_{pq}}{\partial (Y_i^{\mu \nu} \eta_{pq})^L} \right) \frac{\partial \eta_{pq}}{\partial (Y_j^{\mu \nu} \eta_{pq})^L},
\]
where in the last equation we extended the definition of \( \eta_{pq} \)
\[
\eta_{pq} = \sum_{j=1}^{N} \left( i_j - 2r_j - u_j \right).
\]
Application of the above definition leads us to following expression for the electron repulsion integral
\[
ER = \langle \omega_\mu (r_1, r_2, \ldots, r_N) \left| \frac{1}{|r_p - r_q|} \right| \omega_\nu (r_1, r_2, \ldots, r_N) \rangle = \pi \frac{3(N-2)}{2} K_{\mu \nu} \left[ \det (A^{\mu \nu} + B^{\mu \nu}, p, q) \right]^{\frac{3}{2}} \frac{2\pi^{\frac{5}{2}}}{D'(p, q) D''(p, q) + 2b_{pq}^{(N-2)}]}^\times \exp \left[ -\frac{1}{\det (A^{\mu \nu} + B^{\mu \nu}, p, q) \times (R_{1}^{\mu \nu}, \ldots, R_{N}^{\mu \nu}; p, q) S(1, \ldots, N; i, j)(R_{1}^{\mu \nu}, \ldots, R_{N}^{\mu \nu}; p, q)^T \right] \times \exp \left[ -a_{p}^{\mu \nu}(R_{p}^{\mu \nu})^2 - a_{q}^{\mu \nu}(R_{q}^{\mu \nu})^2 \times \prod_{j=1}^{N} \sum_{j, r_{j}, u_{j}} D_{ij, r_{j}, u_{j}}^{(x, pq)} \sum_{k, s_{j}, v_{j}} D_{kj, s_{j}, v_{j}}^{(y, pq)} \sum_{l, t_{j}, u_{j}} D_{lj, t_{j}, u_{j}}^{(z, pq)} \times \sum_{i, p, q, r_{p}, r_{q}, u_{p}, u_{q}} \hat{D}_{i, p, i_{q}, r_{p}, r_{q}, u_{p}, u_{q}} \sum_{i, p, q, r_{p}, r_{q}, u_{p}, u_{q}} \hat{D}_{i, q, i_{p}, r_{p}, r_{q}, u_{p}, u_{q}} \times \sum_{i, p, q, r_{p}, r_{q}, u_{p}, u_{q}} \hat{D}_{i, q, i_{p}, r_{p}, r_{q}, u_{p}, u_{q}, F_{i}(Z)} \right] \times
\]
where the \( D_{ij, r_{j}, u_{j}}^{(x, pq)} \) in the last equation has the following form
\[
D_{ij, r_{j}, u_{j}}^{(x, pq)} = f_{ij, x} (l_{ij, p}^{\mu}, l_{ij, p}^{\nu}, R_{ij, x}^{\mu \nu}, R_{ij, x}^{\mu \nu}, R_{ij, x}^{\mu \nu}, R_{ij, x}^{\mu \nu}) C_{r_{j}}^{l_{ij, p}^{\mu}} \times
\]
\[ \left[ \frac{a_{ij}^{\mu\nu}}{\det(A^{\mu\nu} + B^{\nu\mu}; p, q)} \right]^{i_j - 2r_j - u_j} \left( \begin{array}{c} i_j - 2r_j \\ u_j \end{array} \right) \left[ \frac{\sum_{k=1}^{N} S_{jj}^{(p,q)} g_{j}^{\mu m_k}}{\det(A^{\mu\nu} + B^{\nu\mu}; p, q)} \right]^{\frac{1}{2} n_{pq}} \]

\[ \frac{1}{n_{pq}} \left( \sum_{k=1}^{N} S_{kk}^{(p,q)} g_{k}^{\mu m_k} \right)^{\frac{1}{2} n_{pq}} \times \]

\[ H_{n_{pq}} \left( \frac{\sum_{k=1}^{N} S_{kk}^{(p,q)} g_{k}^{\mu m_k} \tilde{R}_{k,x}^{\mu\nu}}{\det(A^{\mu\nu} + B^{\nu\mu}; p, q) \sqrt{\sum_{k=1}^{N} S_{kk}^{(p,q)} g_{k}^{\mu m_k}}} \right) \times \]

\[ \sum_{l}^{i_j - 2r_j - u_j} \left( \begin{array}{c} i_j - 2r_j - u_j \\ l_j \end{array} \right) \left( \begin{array}{c} b(j(N-3)) \\ j \end{array} \right) \left( \begin{array}{c} b(j(N-3)) \\ j \end{array} \right) \]

\[ (2.143) \]

The term \( \tilde{D}_{i_p, i_q, r_p, r_q, u_p, u_q} \) has a more complicated structure and reads

\[ \tilde{D}_{i_p, i_q, r_p, r_q, u_p, u_q} = \]

\[ \sum_{r_p} \sum_{r_q} \sum_{u_p} \sum_{u_q} C_{i_p}^{i_q} C_{r_p}^{r_q} \left( \begin{array}{c} i_p - 2r_p \\ u_p \end{array} \right) \left( \begin{array}{c} i_q - 2r_q \\ u_q \end{array} \right) \times \]

\[ \left( \sqrt{\frac{1}{2} [D'(p)(a_p^{\mu\nu})^2 + a_p^{\mu\nu}]} \right)^{i_p - 2r_p} \left( \sqrt{\frac{1}{2} [D'(q)(a_q^{\mu\nu})^2 + a_q^{\mu\nu}]} \right)^{i_q - 2r_q} \times \]

\[ \min(i_p - 2r_p, i_q - 2r_q) \sum_{k=0}^{\min(i_p - 2r_p, i_q - 2r_q)} k! \left( \begin{array}{c} i_p - 2r_p \\ k \end{array} \right) \left( \begin{array}{c} i_q - 2r_q \\ k \end{array} \right) \times \]

\[ \left( \frac{2b_{pq}^{(N-2)}a_{p}^{\mu\nu}a_{q}^{\mu\nu}}{\sqrt{[D'(p)(a_p^{\mu\nu})^2 + a_p^{\mu\nu}] [D'(q)(a_q^{\mu\nu})^2 + a_q^{\mu\nu}]}} \right)^{k} \times \]

\[ \sum_{w_1}^{[K_1/2]} \sum_{w_2}^{K_2} \sum_{w_3}^{[w_2/2]} (-1)^{w_1 + w_2 + w_3} \left( K_q - w_1 - K_p + w_2 \right)! \times \]

\[ \left[ \frac{(a_q^{\mu\nu})^2[D'(p) + 2b_{pq}^{\mu\nu(N-2)}]}{[D'(p) + D'(q) + 2b_{pq}^{\mu\nu(N-2)}]} \left( \frac{D'(p) + 2b_{pq}^{\mu\nu(N-2)}}{D'(p, q)} \right) \right]^{w_1} \times \]

\[ \left( \frac{-2a_{p}^{\mu\nu}a_{q}^{\mu\nu}[D'(p) + 2b_{pq}^{\mu\nu(N-2)}][D'(q) + 2b_{pq}^{\mu\nu(N-2)}]}{[D'(p) + D'(q) + 2b_{pq}^{\mu\nu(N-2)}]} \right)^{K_p - w_3} \]
\[
\left[ \frac{-(a_p^{\mu\nu})^2 [D'(q) + 2b_p^{\mu\nu(N-2)}]}{D'(p) + D'(q) + 2b_p^{\mu\nu(N-2)}} \right]^{w_3} \times \sum_{\eta_{pq}} \sum_{L} \left( \sum_{\lambda_1} \sum_{\lambda_2} \sum_{\lambda_3} \sum_{\lambda_4} \sum_{\lambda_5} \sum_{\lambda_6} \right) \times \left( \frac{L - \lambda_1 - \lambda_2}{\lambda_3} \right) \left( \frac{L - \lambda_2 - \lambda_3}{\lambda_4} \right) \times \left( \frac{L - \lambda_1 - \lambda_3}{\lambda_5} \right) \left( \frac{L - \lambda_2 - \lambda_4}{\lambda_6} \right)
\]

\[T_1(\lambda_1, \lambda_2) T_2(\lambda_3, \lambda_4) T_3(\lambda_5, \lambda_6) T_4(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6), \tag{2.144}\]

with

\[T_1(\lambda_1, \lambda_2) = 2^{\lambda_1 + \lambda_2} [D'(p) a_p^{\mu\nu}]^{\lambda_1} (b_p^{(N-2)} a_p^{\mu\nu})^{\lambda_2} (i_p - 2r_p - k - \lambda_1 - \lambda_2)! \times \]

\[H_{i_p - 2r_p - k - \lambda_1 - \lambda_2} \left( \frac{b_p^{(N-2)} a_p^{\mu\nu} Q_{p,x} - D'(p) a_p^{\mu\nu} Q_{p,x} - a_p^{\mu\nu} R_{p,x}}{\sqrt{\frac{1}{2} [D'(p)(a_p^{\mu\nu})^2 + a_p^{\mu\nu}]}} \right), \tag{2.145}\]

\[T_2(\lambda_3, \lambda_4) = 2^{\lambda_3 + \lambda_4} [D'(q) a_q^{\mu\nu}]^{\lambda_3} (b_q^{(N-2)} a_q^{\mu\nu})^{\lambda_4} (i_q - 2r_q - k - \lambda_3 - \lambda_4)! \times \]

\[H_{i_q - 2r_q - k - \lambda_3 - \lambda_4} \left( \frac{b_q^{(N-2)} a_q^{\mu\nu} Q_{q,x} - D'(q) a_q^{\mu\nu} Q_{q,x} - a_q^{\mu\nu} R_{q,x}}{\sqrt{\frac{1}{2} [D'(q)(a_q^{\mu\nu})^2 + a_q^{\mu\nu}]}} \right), \tag{2.146}\]

\[T_3(\lambda_5, \lambda_6) = (-1)^{\lambda_5} \left[ \frac{D'(p) + 2b_p^{(N-2)}}{D'(p, q)} \right]^{\lambda_5} \left[ \frac{D'(q) + 2b_q^{(N-2)}}{D'(p, q)} \right]^{\lambda_6} \times \]

\[
\left( \frac{D'(p) + 2b_p^{(N-2)}}{D'(p, q)} \right) Q_{p,x}^{\mu\nu} - \]

\[
\left[ \frac{D'(q) + 2b_q^{(N-2)}}{D'(p, q)} \right] Q_{q,x}^{\mu\nu} \left[ \zeta_q - K_p - 2w_1 + w_2 + w_3 - \lambda_5 - \lambda_6 \right], \tag{2.147}\]

and

\[T_4(\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6) = \]

\[
\sum_{k_1} \sum_{k_2} \sum_{k_3} \times \]
\[
\frac{(-1)^{k_1+k_2+k_3}(\eta_{pq} - L - \lambda_2 - \lambda_4 - \lambda_6)!}{k_1! \, k_2! \, k_3!} \times \frac{(\eta_{pq} - L - \lambda_2 - \lambda_4 - \lambda_6 - 2k_1)!}{(L - \lambda_1 - \lambda_3 - \lambda_5 - k_2 - 2k_3)!} \times
\]
\[
\left[ \frac{[D'(q) + 2b_{pq}^{\mu\nu}(N-2)]^2}{D'(p) + D'(q) + 2b_{pq}^{\mu\nu}(N-2)} \right]^{k_1} \times \left[ \frac{[D'(q) + 2b_{pq}^{\mu\nu}(N-2)]^2}{D'(p) + D'(q) + 2b_{pq}^{\mu\nu}(N-2)} \right]^{k_3} \times
\]
\[
\left[ \frac{2[D'(q) + 2b_{pq}^{\mu\nu}(N-2)]}{D'(p) + D'(q) + 2b_{pq}^{\mu\nu}(N-2)} \right] L - \lambda_1 - \lambda_3 - \lambda_5 - k_2 - 2k_3 \times
\]
\[
\left( \left[ \frac{D'(p) + 2b_{pq}^{(N-2)}}{D'(p, q)} \right] Q_{p,x}^{\mu\nu} \right) - \left[ \frac{D'(q) + 2b_{pq}^{(N-2)}}{D'(p, q)} \right] Q_{q,x}^{\mu\nu} \eta_{pq} - L - \sum_{i=1}^{6} \lambda_i - 2k_1 - k_2 - 2k_3.
\]

The index \( \epsilon \) in Eq. (2.142) has three components

\[
\epsilon = \epsilon_x + \epsilon_y + \epsilon_z,
\]

where

\[
\epsilon_x = w_1 + w_3 + k_1 + k_3.
\]

Upon examining the above equation one notices that the expression contains a term representing the overlap of the parts of the cluster functions, which depends on the coordinates of the particles not involved in the interaction, and a term representing \( p \) and \( q \) particles involved in the interaction operator.

### 2.8 CONCLUSIONS

The aim of this Chapter was to demonstrate the evaluation of molecular integrals with explicitly correlated multiparticle spherical and Cartesian Gaussian
functions. For the integrals with higher angular momenta we applied the raising operator technique in order to generate appropriate integrals from the integrals over spherical correlated Gaussian functions. The new element introduced in this Chapter is the unitary transformation which allows diagonalization of the quadratic form appearing in the exponent. This approach considerably simplifies the generalization of the integration procedure for an arbitrary number of particles. The size of the matrix which needs to be diagonalized for each integral is not greater than the number of particles involved in the integrated function. It should be pointed out that this procedure should be faster than a procedure based on explicit transformation, such as presented in Lu and Huang paper [88], and should be valid for an arbitrary number of particles.

One can also notice that:

- if we set all correlation parameters equal to zero, the integrals derived here become equal to products of integrals with cartesian orbital Gaussians,

- if we set all correlation parameters and angular quantum numbers equal to zero, one obtains product of integrals with spherical Gaussian orbital,

- in the case of two- and three-particle integrals our formulas lead, after some elementary rearrangements, to expressions derived by Lester and Krauss for Gaussian geminal.
CHAPTER III

EFFECTIVE NONADIABATIC METHOD

3.1 METHODOLOGY

The nonadiabatic wave function expanded in terms of Gaussian cluster functions has been used by Poshusta and co-workers in nonadiabatic calculations on three particle systems [22]. The treatment was recently extended to four particles [79]. Poshusta's approach has been based on the separation of the CM motion from the internal motion through transformation to the CM coordinate system. In our recent work we have taken a different approach which has been based on an effective rather than explicit separation of the CM motion.

To demonstrate the essential points of our approach, let us consider an $N$-particle system with Coulomb interactions. The particle masses and charges are $(m_1, m_2, \ldots m_N)$ and $(Q_1, Q_2, \ldots Q_N)$ respectively. Neglecting the relativistic effects, and in the absence of external fields, the system is described by the Hamiltonian

$$H_{TOT} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{|r_i - r_j|},$$

(3.1)

where $P_i$ and $r_i$ are the positions and momentum vectors. Let us also consider a general coordinate transformation,

$$(r_1, r_2, \ldots, r_N) \rightarrow (R_{CM}, \rho_1, \ldots, \rho_{N-1}),$$

(3.2)

which allows separation of the CM motion from the internal motion, i.e., explicitly separate the total Hamiltonian into the internal Hamiltonian, $H_{Int}$, and the Hamiltonian for the CM motion, $T_{CM} = \frac{p_{CM}^2}{2M}$:

$$H_{TOT} = H_{Int} + T_{CM}.$$ 

(3.3)
Due to this separation, the total wave function can always be represented as a product of the internal part and the wave function for the CM motion

$$\Psi_{\text{TOT}} = \Phi_{\text{CM}} \Phi_{\text{Int}}.$$  \hspace{1cm} (3.4)

Instead of an explicit separation let us now consider the following variational functional:

$$J[\Psi_{\text{TOT}}; k] = \frac{\langle \Psi_{\text{TOT}} | H_{\text{TOT}} | \Psi_{\text{TOT}} \rangle + k \langle \Psi_{\text{TOT}} | T_{\text{CM}} | \Psi_{\text{TOT}} \rangle}{\langle \Psi_{\text{TOT}} | \Psi_{\text{TOT}} \rangle},$$  \hspace{1cm} (3.5)

where $k$ is an arbitrary constant which scales the positive term that represents the kinetic energy of the motion of the center of mass. Both operators, i.e., the total Hamiltonian, $H_{\text{TOT}}$, and the kinetic energy of the CM motion, $T_{\text{CM}}$, have simple forms in the Cartesian coordinate system. By minimizing the functional $J[\Psi_{\text{TOT}}, k]$ with positive values for $k$, the kinetic energy of the CM motion can be forced to become much smaller than the internal energy of the system. In order to perform a meaningful nonadiabatic variational calculation the kinetic energy contributions need to be reduced and made as insignificant as possible in comparison to the internal energy. For larger $k$ values, more emphasis in the optimization process is placed on reducing the magnitude of $\frac{\langle \Psi_{\text{TOT}} | T_{\text{CM}} | \Psi_{\text{TOT}} \rangle}{\langle \Psi_{\text{TOT}} | \Psi_{\text{TOT}} \rangle}$. In our own calculations the value for $k$ has been selected based on the accuracy we wanted to achieve in determining the internal energy of the system. The approach based on minimizing the expectation value of $T_{\text{CM}}$ will be called Method I in our further discussion.

There is an alternative scheme to nonadiabatic calculation we’ll call Method II. Let us examine the case when the $k$ parameter is set to $-1$ in Eq.(3.5). The functional becomes

$$J[\Psi_{\text{TOT}}; -1] = \frac{\langle \Psi_{\text{TOT}} | H_{\text{TOT}} - T_{\text{CM}} | \Psi_{\text{TOT}} \rangle}{\langle \Psi_{\text{TOT}} | \Psi_{\text{TOT}} \rangle} = \frac{\langle \Psi_{\text{TOT}} | H_{\text{Int}} | \Psi_{\text{TOT}} \rangle}{\langle \Psi_{\text{TOT}} | \Psi_{\text{TOT}} \rangle}.$$  \hspace{1cm} (3.6)

The full optimization effort can now be directed solely to improving the internal energy of the system because the functional Eq.(3.6) now represents only the internal Hamiltonian. One can expect that after optimization the variational wave function will be a sum of products of the internal ground state and wave functions representing
different states of the CM motion:

\[ \Psi_{TOT} = \Phi_{Int} \sum_i a_i \phi^i_{cm}. \]  

(3.7)

However, since the internal Hamiltonian only acts on the internal wave function, the variational functional, \( J[\Psi_{TOT}; -1] \), becomes

\[ \min \{ J[\Psi_{TOT}; -1] \} = \min \left\{ \frac{\langle \Phi_{Int} | H_{TOT} - T_{CM} | \Phi_{Int} \rangle}{\langle \Phi_{Int} | \Phi_{Int} \rangle} \right\}, \]

(3.8)

which according to the variational principle is

\[ \min \{ J[\Psi_{TOT}; -1] \} \geq E_{Int}. \]

(3.9)

Therefore in Method II, by minimization of the functional Eq.(3.6), one obtains directly an upper bound to the internal energy of the system. In this case the kinetic energy of the CM motion is not minimized.

In the above considerations we demonstrated that the internal energy can be separated from the total energy of the system without an explicit transformation to the CM coordinate system. This is an important point since an inappropriate elimination of the CM can lead to so-called “spurious” states [44], which in turn can lead to contradictory results in nonadiabatic calculations.

The last element which we would like to demonstrate is that the variational wave function in the form which was introduced in the previous Chapter can be formally separated into a product of an internal wave function and a wave function of the CM motion. This is mandatory for any variational nonadiabatic wave function in order to provide required separability of the internal and external degrees of freedom. To demonstrate this let us consider an \( N \)-particle system with masses \( m_1, m_2, \ldots, m_N \). An example of a wave function for this system which separates to a product of the internal and external components is

\[ \Psi_{TOT} = \exp(-\eta R_{CM}^2) \sum_k C_k \exp \left( - \sum_{i=1}^{N} \sum_{j>i}^{N} \gamma_{ij} r_{ij}^2 \right). \]

(3.10)
It can be shown that with the use of the matrices

\[ \tilde{M} = \frac{\eta}{M^2} \begin{pmatrix} \sum_{j=1}^{N} \gamma_{1j}^k & -\gamma_{12}^k & \cdots & -\gamma_{1N}^k \\ -\gamma_{12}^k & \sum_{j=1}^{N} \gamma_{2j}^k & \cdots & -\gamma_{2N}^k \\ \vdots & \vdots & \ddots & \vdots \\ -\gamma_{1N}^k & -\gamma_{2N}^k & \cdots & \sum_{j=1}^{N} \gamma_{Nj}^k \end{pmatrix}, \]  

(3.11)

and

\[ \Gamma_k = \begin{pmatrix} m_1^2 & m_1m_2 & \cdots & m_1m_N \\ m_1m_2 & m_2^2 & \cdots & m_2m_N \\ \vdots & \vdots & \ddots & \vdots \\ m_1m_N & m_2m_N & \cdots & m_N^2 \end{pmatrix} \]  

(3.12)

the total wave function, \( \Psi_{TOT} \), can be represented as

\[ \Psi_{TOT} = \sum_k C_k \exp \left( -\langle r_1, r_2, \ldots, r_N \rangle (\tilde{M} + \Gamma_k)(r_1, r_2, \ldots, r_N) \right), \]  

(3.13)

which has the same form as the many body wave function with \( R_i^k = 0 \) and \( A_{ij}^k = \delta_{ij} \alpha_i^k \), i.e.,

\[ \Psi_{TOT} = \sum_k C_k \exp \left( -\langle r_1, r_2, \ldots, r_N \rangle (A^k + B^k)(r_1, r_2, \ldots, r_N) \right). \]  

(3.14)

The main idea of the above presented methodology rests in treating nonadiabatically the \( N \)-particle problem in the Cartesian space without reducing it to an \((N-1)\)-particle problem by explicit separation of the CM motion. One can ask what advantages does this approach have in comparison to the conventional one? One clear advantage is that we avoid selecting an internal coordinate system \(-\) a procedure that is not unique and may lead to certain ambiguities. The work in Cartesian space makes the physical picture more intuitive and the required multiparticle integrals are much easier to evaluate. Those two features certainly are not present in more complicated coordinate systems such as in polyspherical coordinates [45]. Also, we noted earlier that the other factor which should be taken into consideration is the proper “ansatz” for the trial variational wave function incorporating the required permutational symmetry. In our approach the appropriate permutational symmetry is easy to implement through direct exchange of the particles in the orbital factors.
and the correlation components. This task, however, can be complicated when one works with a transformed coordinate system. The last problem which should be taken into consideration relates to the rotational properties of the wave function. Definitions of the appropriate rotational operators in terms of the Cartesian coordinates are straightforward, as we will show in one of the following Chapters. In a transformed coordinate system, however, the operators representing the rotation of the system about its CM can be complicated and may lead to significant difficulties in calculating the required matrix elements.

3.2 NUMERICAL EXAMPLES

The effective nonadiabatic method presented in the last section was computationally implemented and some results have been obtained for two-, three-, and four-body systems. In discussing the numerical results we will make comparisons with exact values, if available, or with the best results available in the literature. We will also discuss how the present approach can be applied to bigger systems.

Consider first our numerical results for the model system of the positronium. The positronium system \((e^+e^-)\) is strongly nonadiabatic and presents an ideal simple test case since its nonrelativistic ground state energy can be determined exactly \((E_{g.s.} = -0.25a.u.)\).

In our calculations for the positronium system we used the following fourteen-term variational wave function:

\[
\Psi_{TOT} = \sum_{i=1}^{14} C_i \exp\left(-\alpha_i r_1^2 - \alpha_i' r_2^2 - \beta_i r_1 r_2 \right) \Theta(e^-) \Theta(e^+). \tag{3.15}
\]

The minimization of the variational functional Eq.(3.5) was performed with different values of \(k\). The results of the calculations are summarized in Table I.

In the calculation employing Method II \((k = -1)\) we obtained an internal energy almost identical to the exact nonrelativistic ground state energy. The energy of the CM motion in these calculations converged to a rather small value of \(5.0135 \times 10^{-5}\) a.u. In the calculations with Method I, this energy was reduced two-fold by
TABLE I. Ground state energies computed with different $k$ values for the $e^+e^-$. Energies in atomic units.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$\min{J[\Psi;k]}$</th>
<th>$E_{Int}^{a)}$</th>
<th>$T_{CM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.2499470</td>
<td>-0.2499695</td>
<td>2.2524$x10^{-5}$</td>
</tr>
<tr>
<td>100</td>
<td>-0.2489623</td>
<td>-0.2496026</td>
<td>6.4036$x10^{-6}$</td>
</tr>
<tr>
<td>-1</td>
<td>-0.2499962</td>
<td>-0.2499962</td>
<td>5.0135$x10^{-5}$</td>
</tr>
</tbody>
</table>

Method I

Method II

$E_{Int}^{a)} = \min\{J[\Psi,-1]\}$,

For Method I $E_{Int} = \min\{J[\Psi,0]\}$.

using the value of the penalty parameter $k$ equal to 1.0 and almost ten-fold by using the value of the penalty parameter $k$ equal to 100. By enforcing minimization of $\langle T_{CM} \rangle$, we obtained a somewhat higher value of the internal energy. This can be corrected by using a longer expansion for the wave function. In conclusion, we can say that the Gaussian cluster functions can fairly well represent a nonadiabatic system with Coulombic interactions. It seems that both Method I and Method II provide similar results mainly dependent on the length of the expansion of the wave function. However, for the same expansion length, Method II seems to perform better and converge faster.

Consider now the three-body system, the $H_2^+$ molecule, where particles interact again via Coulombic forces but masses of particles are significantly different.
This system has been extensively studied in the past by a number of researchers [21,22,26,37,43]. The nonadiabatic ground state wave function for this system is assumed to be

$$\Psi_{TOT}(A, B, 1) = \sum_{k=1}^{M} C_k P(A, B)[\omega_k(A, B, 1)]\Theta(A, B)\Theta(1),$$

where

$$\omega_k(A, B, 1) = \exp \left[ -\alpha_A^k r_A^2 - \alpha_B^k r_B^2 - (r_A, r_B, r_1)B^k(r_A, r_B, r_1)^T \right],$$

and $r_A$ and $r_B$ are the respective distances of particles A and B from the center of the coordinate system. The spin function $\Theta(1)$ for the electron can be either $\alpha(1)$, or $\beta(1)$, and the spin function for the nuclei, $\Theta(A, B)$, is the singlet function $\frac{1}{\sqrt{2}}[\alpha(A)\beta(B) - \alpha(B)\beta(A)]$. We assume that the coupling between the electron spin and spin of the nuclei is negligibly small. The matrix $B^k$ is a combination of nonlinear parameters

$$B^k = \begin{pmatrix}
\beta_{AB}^k + \beta_{A1}^k & -\beta_{AB}^k & -\beta_{A1}^k \\
-\beta_{AB}^k & \beta_{AB}^k + \beta_{B1}^k & -\beta_{B1}^k \\
-\beta_{A1}^k & -\beta_{B1}^k & \beta_{A1}^k + \beta_{B1}^k
\end{pmatrix}.$$
\[ \beta_{12}^k = A_{12} \exp(B_{12}(k,1) + C_{12}(k,2)), \]
\[ \beta_{13}^k = A_{13} \exp(B_{13}(k,3) + C_{13}(k,4)), \]
\[ \beta_{23}^k = A_{23} \exp(B_{23}(k,5) + C_{23}(k,6)), \]

with
\[ \langle k, j \rangle = \text{fractional part of } \left[ \frac{1}{2} k(k+1) \right] P(j)^{\frac{1}{2}} \],

and \( P(j) \) is the \( j \)-th prime number in the sequence \( 2, 3, 5, 7 \ldots \). This approach considerably reduces the number of optimized parameters.

We performed variational calculations using short expansions and successively added more functions using as the starting point the parameters from the previous optimization. At first we used the variational functional with the value of the penalty factor, \( k \), equal to zero. Our results for different numbers of Gaussians clusters in the expansion are listed in Table II.

**TABLE II.** Ground state energies computed with a basis set of \( M \) functions for the \( H_2^+ \) molecule*.

<table>
<thead>
<tr>
<th>( M )</th>
<th>Ref. 22</th>
<th>( E_{Tot} )</th>
<th>( E_{CM} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-0.5599</td>
<td>-0.563787</td>
<td>0.1072 \times 10^{-2}</td>
</tr>
<tr>
<td>8</td>
<td>-0.5706</td>
<td>-0.575483</td>
<td>0.8795 \times 10^{-2}</td>
</tr>
<tr>
<td>16</td>
<td>-0.57736</td>
<td>-0.583609</td>
<td>0.2698 \times 10^{-2}</td>
</tr>
<tr>
<td>32</td>
<td>-0.58920</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-0.592896</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>-0.591096</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>-0.594304</td>
<td></td>
<td></td>
</tr>
<tr>
<td>256</td>
<td>-0.596030</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The best literature value = -0.59713906 [43].
For comparison we tabulated the results of Poshusta [22] who also used a Gaussian expansion for the wave function, but separated the internal and external degrees of freedom in the Hamiltonian. Poshusta’s results provide a good reference for our calculations since he also applied a similar tempering procedure in the minimization of the nonlinear parameters. Upon comparing our’s and Poshusta’s total energies one notices that our results are consistently below Poshusta’s values for similar expansion lengths. This behaviour is anticipated after considering that our variational wave functions contain more variational parameters. However, our total energy contains an additional, though very small, positive contribution from the CM motion which is absent in Poshusta’s results.

According to our previous discussion we should be able to reduce the contribution from the external motion to the total energy by employing the modified variational procedure, Eq.(3.5), which includes the penalty term proportional to the expectation value of the kinetic energy of the CM motion. In order to test the procedure we performed variational calculations with different values set for parameter k, namely 0.5, 1, 10 and 100. Table III contains results of these calculations.

TABLE III. Ground state energies computed with different k values for $H_2^+$ molecule.

<table>
<thead>
<tr>
<th>M</th>
<th>k values</th>
<th>$E_{TOT}$</th>
<th>$E_{CM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.5</td>
<td>-0.571092</td>
<td>0.6453$\times 10^{-3}$</td>
</tr>
<tr>
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<td>1</td>
<td>-0.570831</td>
<td>0.2998$\times 10^{-5}$</td>
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<tr>
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<td>-0.567395</td>
<td>0.1387$\times 10^{-5}$</td>
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<td>0.8170$\times 10^{-6}$</td>
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<td>0.4209$\times 10^{-6}$</td>
</tr>
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<td></td>
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</tr>
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<td>0.5739$\times 10^{-4}$</td>
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<td>0.7263$\times 10^{-6}$</td>
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<tr>
<td></td>
<td>100</td>
<td>-0.592039</td>
<td>0.2936$\times 10^{-6}$</td>
</tr>
</tbody>
</table>
Upon examining the values of \( \langle T_{CM} \rangle \) one notices a significant decrease of this quantity by several orders of magnitude in comparison with the corresponding values obtained without the penalty term on the variational functional. One also notices that the calculated variational total energies are slightly higher in comparison to the corresponding total energies as one may have expected since the optimization procedure shifts its emphasis more towards minimization of \( \langle T_{CM} \rangle \). Upon examining the results obtained with different values of \( k \) we can conclude that \( k=1 \) already sufficiently reduces the contribution from the kinetic energy of the CM motion.

We also performed a series of calculations for a sequence of simple systems, \( H, H_2^+ \) and \( H_2 \). The results are in Table IV.

### TABLE IV. Nonadiabatic calculations on \( H, H_2^+ \) and \( H_2 \) accomplished with Method II.

<table>
<thead>
<tr>
<th>No. of Gaussian clusterfunctions</th>
<th>( E_{Int} )</th>
<th>Exact or best literature value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-0.499724</td>
<td>-0.499729</td>
</tr>
<tr>
<td>( H_2^+ )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>-0.559387</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-0.590105</td>
<td></td>
</tr>
<tr>
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<td>-0.594571</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>-0.596257</td>
<td></td>
</tr>
<tr>
<td>( H_2 )</td>
<td></td>
<td>-0.597139 \cite{43}</td>
</tr>
<tr>
<td>16</td>
<td>-1.142988</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>-1.148156</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>-1.155322</td>
<td>-1.164024 \cite{43}</td>
</tr>
</tbody>
</table>
The question one may ask is how many Gaussian cluster functions are necessary to obtain satisfactory results for those systems. Notice that with a short expansion we almost reproduced the exact nonrelativistic energy for the hydrogen atom. It takes only about 16 Gaussian cluster functions to lower the energy below $-0.59 \text{a.u.}$ for the $H_2^+$ molecule, and with 64 functions one gets already within 0.0009a.u. to the best nonrelativistic result of $-0.597139$ [43]. For $H_2$, which consists of four particles, we did calculations with 16, 28 and 56 cluster functions. The results indicate that one should use at least 300 or more to obtain a result of comparable accuracy as achieved for $H_2^+$.

The nonadiabatic wave function representing the ground state energy of the $H_2$ molecule has the following form:

$$\Psi_{TOT}(A, B, 1, 2) =$$

$$\sum_{k=1}^{M} C_k P(A, B) P(1, 2) \omega_k (r_A, r_B, r_1, r_2) \Theta(A, B) \Theta(1, 2),$$

(3.21)

where $A, B$ are protons and 1, 2 are electrons. We assumed coupling between nuclear and electron spins was negligible and, therefore, the spin function of the system is a product of the spin functions for the nuclei and the electrons. For the ground state, both spin functions $\Theta(A, B)$ and $\Theta(1, 2)$ represent singlet states. Therefore if the $\hat{O}$ operator is permutationally invariant its matrix element is calculated as follows:

$$\langle P(A, B) P(1, 2) \omega_l \Theta(A, B) \Theta(1, 2) | \hat{O} | \omega_k \Theta(A, B) \Theta(1, 2) \rangle =$$

$$\langle \omega_l (r_A, r_B, r_1, r_2) | \hat{O} | \omega_k (r_A, r_B, r_1, r_2) \rangle +$$

$$\langle \omega_l (r_B, r_A, r_1, r_2) | \hat{O} | \omega_k (r_A, r_B, r_1, r_2) \rangle +$$

$$\langle \omega_l (r_A, r_B, r_2, r_1) | \hat{O} | \omega_k (r_A, r_B, r_1, r_2) \rangle +$$

$$\langle \omega_l (r_B, r_A, r_2, r_1) | \hat{O} | \omega_k (r_A, r_B, r_1, r_2) \rangle.$$  

(3.22)

The spatial part becomes

$$\omega_k = \exp \left[ -(r_A, r_B, r_1, r_2)(A^k + B^k)(r_A, r_B, r_1, r_2)^T \right],$$

(3.23)
where the matrix \((A^k + B^k)\) contains four orbital exponents in the diagonal positions and six correlation exponents. In such expansions all parameters, \textit{i.e.}, orbital and correlation exponents) are subject to optimization. This creates a problem one often encounters in variational nonadiabatic calculations for more extended systems with a larger number of basis functions: the necessity to optimize many non-linear parameters. The next two Chapters outline the approach we have taken to overcome this problem.
CHAPTER IV

GRADIENT TECHNIQUE

4.1 METHODOLOGY

The number of nonlinear parameters in the wave function introduced in the previous Chapter increases very rapidly with the length of the expansion, and the optimization procedure becomes very expensive. In our previous calculations we used an iterative two-step procedure. For a given basis set defined by a set of nonlinear parameters, we solved the standard secular equation, $HC = SCE$, determining the linear coefficients. We then used the conjugate gradient method and the random tempering procedure to determine the nonlinear parameters. The above two steps were repeated until the energy converged below the assumed threshold. Even when the set of the optimized parameters is not very big, and the expansion is not very long, the optimization procedure takes a long time. This is due to the fact that the collective motion of all particles is strongly correlated and this leads to a strong coupling between the nonlinear parameters.

In this Chapter we would like to propose an application of the analytical first derivatives of the variational functional with respect to the nonlinear parameters of the wave function in order to make the optimization more efficient. The technique of analytical derivatives presented here is quite general and can be applied to different quantum mechanical problems where explicitly correlated Gaussian functions are used. Let $X(\xi_1, \xi_2, ..., \xi_n)$ be the n-dimensional vector of the nonlinear parameters, i.e., both orbital and correlation exponents. The Taylor expansion about point $X^*$ of the functional, Eq.(3.5), can be obtained as follows:
\[ J[X; k] = J[X^*; k] + \sum_{i=1}^{n} \frac{\partial J[X; k]}{\partial \xi_i} \bigg|_{x^*} (\xi_i - \xi^*_i) + \]
\[ \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{\partial^2 J[X; k]}{\partial \xi_i \partial \xi_j} \bigg|_{x^*} (\xi_i - \xi^*_i)(\xi_j - \xi^*_j) + \ldots \quad (4.1) \]

or, in the matrix form

\[ J[X; k] = \]
\[ J[X^*; k] + (X - X^*)^T \nabla J[X; k] \bigg|_{x^*} + \frac{1}{2} (X - X^*)^T H \bigg|_{x^*} (X - X^*) + \ldots, \quad (4.2) \]

where \( H \bigg|_{x^*} = \nabla \nabla^T J[X; k] \bigg|_{x^*} \) denotes the Hessian evaluated at the \( X^* \) point. At the minimum point the gradient becomes equal to zero, \( \nabla J[X; k] \big|_{x^*} = 0 \), and as \(|X - X^*|\) approaches zero, the expansion (4.2) becomes dominated by the quadratic term. If the Hessian matrix is positive definite, then the quadratic approximation will have its minimum at \( X^* \). The quadratic convergence will be assumed here to find the minimum of functional (3.5). Let us consider the first derivative of the functional \( J[\{\alpha^i_p\}, \{\beta^i_pq\}; k] \) with respect to an arbitrary parameter \( \xi \),

\[ \frac{\partial}{\partial \xi} J[\{\alpha^i_p\}, \{\beta^i_pq\}; k] = \]
\[ \frac{1}{\langle \Psi_{TOT}|\Psi_{TOT} \rangle} \left[ \frac{\partial}{\partial \xi} \langle \Psi_{TOT}|H|\Psi_{TOT} \rangle + k \frac{\partial}{\partial \xi} \langle \Psi_{TOT}|T_{CM}|\Psi_{TOT} \rangle \right] - \]
\[ J[\{\alpha^i_p\}, \{\beta^i_pq\}; k] \frac{1}{\langle \Psi_{TOT}|\Psi_{TOT} \rangle} \frac{\partial}{\partial \xi} \langle \Psi_{TOT}|\Psi_{TOT} \rangle, \quad (4.3) \]

where \( \xi \) can be \( \alpha^i_p \) or \( \beta^i_pq \). As mentioned above, the set of linear coefficients is obtained by solving the secular equation. This set is not optimal with respect to the variational functional \( J \) because \( J \) contains an additional term \( \langle \Psi_{TOT}|T_{CM}|\Psi_{TOT} \rangle \), which is not present in the secular equation. However, the set becomes optimal if \( k \) is set to zero or when the kinetic energy of the center-of-mass motion vanishes. Therefore, the smaller the \( \langle \Psi_{TOT}|T_{CM}|\Psi_{TOT} \rangle \) term is, the more fulfilled the condition

\[ \frac{\partial}{\partial \xi} J[\{\alpha^i_p\}, \{\beta^i_pq\}; k] \approx 0 \quad (4.4) \]
should become. To make the Eq.(4.3) more explicit, let us consider a matrix element with the function given in terms of explicitly correlated Gaussian functions

$$
\langle \Psi_{TOT} | \hat{O} | \Psi_{TOT} \rangle = \sum_{i=1}^{M} \sum_{k=1}^{M} C_i C_k \{ P[\omega_l \Theta_{S,M}^N] | \hat{O} | \omega_k \Theta_{S,M}^N \},
$$

where $\hat{O} = H_{TOT}, T_{CM}$ or 1. Differentiating with respect to $\xi^k$, i.e., a nonlinear parameter of the $\omega_k$ basis function, one obtains

$$
\frac{\partial}{\partial \xi^k} \langle \Psi_{TOT} | \hat{O} | \Psi_{TOT} \rangle = \sum_{i=1}^{M} (1 + \delta_{ik}) C_i C_k \{ P[\omega_l \Theta_{S,M}^N] | \hat{O} | \omega_k \Theta_{S,M}^N \}.
$$

As mentioned before, we consider the case where all orbital centers $R_i^k$ coincide with the center of the coordinate system. Introducing the diagonal matrix $A^k$ of orbital exponents, the expression for $\omega_k$ becomes

$$
\omega_k = \exp \left[ -r(A^k + B^k)r^T \right],
$$

and all required integrals can be expressed in terms of the $(A^k + B^k)$ matrix elements.

Before we demonstrate the evaluation of the integral derivatives, let us consider the determinant of the $(A^k + B^k)$ matrix and its derivative with respect to the nonlinear parameters. The determinant, $det(A^k + B^k)$, can be expanded with respect to the p’th column

$$
det(A^k + B^k) = \sum_{i=1}^{N} (-1)^{i+p}(a + b)_{i,p} \{(A^k + B^k)_{i,p}\}.
$$

Differentiation with respect to $\alpha_{p}^k$ gives

$$
\frac{\partial}{\partial \alpha_{p}^k} det(A^k + B^k) = det(A^k + B^k|_{1,p}).
$$

The notation $det(A^k + B^k|_{1,p})$ means that the $p$’th column and $p$’th row are set to zero, and the $(A^k + B^k)_{p,p}$ element is set equal to 1. Additionally, $det(A^l)$ denotes $det(A^l + A^k)$, and similarly for $det(B^l)$. The differentiation with respect to $b_{pq}^k$,
appearing in the diagonal elements, can be carried out in a similar way. For the off-diagonal elements one needs to multiply the expression by a factor of 2,

$$\frac{\partial}{\partial b_{pq}^k} \det(A^k + B^k) = (2 - \delta_{pq}) \det(A^k + B^k|1_{pq}).$$  \hspace{1cm} (4.10)$$

The last required differentiation, with respect to \( \beta^k_{pq} \), can be transformed to differentiation with respect to \( b_{pq}^k \) using the chain rule:

$$\frac{\partial}{\partial \beta^k_{pq}} =$$

\[
\left( \frac{\partial b_{ii}^k}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b_{ii}^k} + \left( \frac{\partial b_{ij}^k}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b_{ij}^k} + \left( \frac{\partial b_{ij}^k}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b_{ij}^k} + \left( \frac{\partial b_{ij}^k}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b_{ij}^k}. \hspace{1cm} (4.11)$$

For \( \beta^k_{pq} \), subscript \( p \) is always different than \( q \). Upon examining the structure of the matrix \( B^k \), one obtains

$$\frac{\partial b_{ij}^k}{\partial \beta^k_{pq}} = (1 + \delta_{lk}) \Delta(i, j; p, q),$$  \hspace{1cm} (4.12)$$

where

$$\Delta(i, j; p, q) = \delta_{ij}(\delta_{ip} + \delta_{jq}) - (\delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}).$$  \hspace{1cm} (4.13)$$

Using the above relation, Eq.(4.11) simplifies

$$\frac{\partial}{\partial \beta^k_{pq}} = (1 + \delta_{lk}) \left[ \frac{\partial}{\partial b_{ii}^k} + \frac{\partial}{\partial b_{ij}^k} - \frac{\partial}{\partial b_{ij}^k} - \frac{\partial}{\partial b_{ij}^k} \right],$$  \hspace{1cm} (4.14)$$

and differentiation with respect to \( \beta^k_{pq} \) can be easily evaluated

$$\frac{\partial}{\partial \beta^k_{pq}} \det(A^k + B^k) = (1 + \delta_{lk})[\det(A^k + B^k|1_{pp}) + \det(A^k + B^k|1_{qq})$$

$$- 2 \det(A^k + B^k|1_{pq})],$$  \hspace{1cm} (4.15)$$

because matrix \( A^k + B^k \) is symmetric.
4.2 DERIVATIVES OF MOLECULAR INTEGRALS WITH RESPECT TO NONLINEAR PARAMETERS

In this section we demonstrate the derivatives of one-center multiparticle integrals over explicitly correlated Gaussian functions with respect to the nonlinear parameters. Appropriate formulas are tabulated below:

\begin{equation}
\langle \omega_l(r_1, r_2, \ldots, r_N)|\omega_k(r_1, r_2, \ldots, r_N) \rangle = \pi^{\frac{3N}{2}} [\text{det}(A^{lk} + B^{lk})]^{-\frac{3}{2}} \quad (4.16)
\end{equation}

First derivative with respect to $\xi$

\begin{equation}
\langle \omega_l(r_1, r_2, \ldots, r_N)|\frac{\partial}{\partial \xi} \omega_k(r_1, r_2, \ldots, r_N) \rangle
= -\frac{3}{2} \langle \omega_l|\omega_k \rangle \frac{1}{\text{det}(A^{lk} + B^{lk})} \frac{\partial}{\partial \xi} \text{det}(A^{lk} + B^{lk}) \quad (4.17)
\end{equation}

when

a) $\xi = \alpha^k_p$;

\[ \frac{\partial}{\partial \alpha^k_p} \text{det}(A^{lk} + B^{lk}) = (1 + \delta_{lk})\text{det}(A^{lk} + B^{lk}|1_{pp}), \]

and when

b) $\xi = \beta^k_{pq}$;

\[ \frac{\partial}{\partial \beta^k_{pq}} \text{det}(A^{lk} + B^{lk}) = (1 + \delta_{lk}) [\text{det}(A^{lk} + B^{lk}|1_{pp}) + \text{det}(A^{lk} + B^{lk}|1_{qq}) - 2\text{det}(A^{lk} + B^{lk}|1_{pq})]. \]
Kinetic energy integral

Before we demonstrate the derivative of the kinetic energy integral, let us consider the following integral

$$I_{ij}^{lk} = \int \ldots \int [\nabla_i \omega_l(r_1, r_2, \ldots r_N)][\nabla_j \omega_k(r_1, r_2, \ldots r_N)] dr_1 dr_2 \ldots dr_N. \quad (4.18)$$

For the nonadiabatic wave function given when all orbital centers coincide with the center of the coordinate system, integral $I_{ij}^{lk}$ becomes

$$I_{ij}^{lk} = 4 \left[ \alpha_i^j \alpha_j^k J(r_i, r_j; 1, 1) + \alpha_i^l \sum_{s=1}^N b_{js}^k J(r_i, r_s; 1, 1) \right. \left. + \alpha_j^k \sum_{m=1}^N b_{im}^l J(r_j, r_m; 1, 1) + \sum_{m=1}^N \sum_{s=1}^N b_{im}^l b_{js}^k J(r_m, r_s; 1, 1) \right]. \quad (4.19)$$

where $J(r_p, r_q; n_1, n_2)$ is the generalized overlap integral

$$J(r_p, r_q; n_1, n_2) =$$

$$\int \ldots \int r_p^{n_1} r_q^{n_2} \exp \left( - \sum_{n=1}^N a_{n}^{lk} |r_n - R_n^{lk}|^2 - r_B^{lk} r_T \right) dr_1 dr_2 \ldots dr_N, \quad (4.20)$$

as we demonstrated previously. It is more convenient for calculation of derivatives to rewrite Eq.(4.19) in the following form:

$$I_{ij}^{lk} = 4 \sum_{m=1}^N \sum_{s=1}^N (\alpha_i^j \delta_{mi} + b_{im}^l)(\alpha_j^k \delta_{sj} + b_{js}^k) J(r_m, r_s; 1, 1). \quad (4.21)$$

The integral with $n_1 = n_2 = 1$ can be calculated as a partial derivative of the overlap integral with respect to the nonlinear correlation parameter, $b_{pq}^{lk}$,

$$J(r_p, r_q; 1, 1) = \frac{-1}{2 - \delta_{pq}} \frac{\partial}{\partial b_{pq}^{lk}} (\omega_l \omega_k), \quad (4.22)$$

where $\delta_{sm}$ is the Kronecer delta. Using the expression for $J(r_p, r_q; 1, 1)$, integral $I_{ij}^{lk}$ becomes
Further simplification can be made by introducing the expression for the first derivative of the overlap integral

\[ I_{ij}^{l_k} = -4 \sum_{m=1}^{N} \sum_{s=1}^{N} (\alpha_m^l \delta_{mi} + b_{im}^l)(\alpha_s^k \delta_{sj} + b_{js}^k) \left( \frac{1}{2 - \delta_{ms}} \right) \frac{\partial}{\partial b_{lk}_{ms}} \langle \omega_l | \omega_k \rangle. \] (4.23)

Using the integral \( I_{ij}^{l_k} \), the kinetic energy matrix element reads

\[ T_{lk} = \frac{1}{2} \sum_{i=1}^{N} \frac{1}{m_i} I_{ii}^{l_k}, \] (4.26)

which together with Eq.(4.24) allows us to rewrite the kinetic energy integral in a more compact form:

\[ T_{lk} = 3 \frac{\langle \omega_l | \omega_k \rangle}{\det(A^{lk} + B^{lk})} \sum_{i=1}^{N} \frac{1}{m_i} W_{ii}. \] (4.27)

The matrix element for the kinetic energy of the center-of-mass motion

\[ (T_{CM})_{lk} = \frac{1}{2M} \sum_{i=1}^{N} \sum_{j=1}^{N} I_{ij}^{l_k}, \] (4.28)

where \( M = \sum_{i=1}^{N} m_i \), can be obtained in a similar way:

\[ (T_{CM})_{lk} = 3 \frac{\langle \omega_l | \omega_k \rangle}{M \det(A^{lk} + B^{lk})} \sum_{i=1}^{N} \sum_{j=1}^{N} W_{ij}. \] (4.29)
The first derivative with respect to $\xi$ can now be calculated as:

$$\frac{\partial}{\partial \xi} T_{lk} = -\frac{5}{2} \frac{T_{lk}}{\det(A^{lk} + B^{lk})} \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk})$$

$$+ \frac{3\langle \omega_l | \omega_k \rangle}{\det(A^{lk} + B^{lk})} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial}{\partial \xi} W_{ii},$$

and simplified using the formula for the derivative of the overlap integral

$$\frac{\partial}{\partial \xi} T_{lk} = \frac{5}{3} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) + \frac{3\langle \omega_l | \omega_k \rangle}{M \det(A^{lk} + B^{lk})} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\partial \xi} W_{ij}. \quad (4.31)$$

The derivative of the kinetic energy integral can be found in a similar way:

$$\frac{\partial}{\partial \xi} (T_{CM})_{lk} =$$

$$\frac{5}{3} \frac{(T_{CM})_{lk}}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) + \frac{3\langle \omega_l | \omega_k \rangle}{M \det(A^{lk} + B^{lk})} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{\partial \xi} W_{ij}. \quad (4.32)$$

The appropriate derivatives are listed below:

a) $\xi = \alpha^k_p$:

$$\frac{\partial}{\partial \alpha^k_p} W_{ij} = (1 + \delta_{lk}) \sum_{m=1}^{N} \sum_{s=1}^{N} (\alpha_m^l \delta_{mi} + b_{im}^l) \left[ \delta_{sp} \delta_{sj} \det(A^{lk} + B^{lk} | 1_{ms}) \right.$$

$$+ (1 + \delta_{lk})(\alpha_s^k \delta_{sj} + b_{js}^k) \det(A^{lk} + B^{lk} | 1_{ms}, 1_{pp})(1 - \delta_{mp})(1 - \delta_{sp})],$$

b) $\xi = \beta_{pq}^k$:

$$\frac{\partial}{\partial \beta_{pq}^k} W_{ij} = (1 + \delta_{lk}) \sum_{m=1}^{N} \sum_{s=1}^{N} (\alpha_m^l \delta_{mi} + b_{im}^l) \left[ \Delta(j, s; p, q) \det(A^{lk} + B^{lk} | 1_{ms}) \right.$$

$$+ (1 + \delta_{lk})(\alpha_s^k \delta_{sj} + b_{js}^k) \left[ \det(A^{lk} + B^{lk} | 1_{ms}, 1_{pp})(1 - \delta_{mp})(1 - \delta_{sp}) \right.$$

$$+ \det(A^{lk} + B^{lk} | 1_{ms}, 1_{qq})(1 - \delta_{mq})(1 - \delta_{sq})$$

$$- \det(A^{lk} + B^{lk} | 1_{ms}, 1_{pq})(1 - \delta_{mp})(1 - \delta_{sq})$$

$$- \det(A^{lk} + B^{lk} | 1_{ms}, 1_{qp})(1 - \delta_{mq})(1 - \delta_{sp})].$$
Two-body Coulomb integral

The two-body Coulomb integral, evaluated previously, has the form

\[
\langle \omega_l(r_1, r_2, \ldots, r_N) | \frac{1}{|r_i - r_j|} | \omega_k(r_1, r_2, \ldots, r_N) \rangle = \pi \frac{3(N-2)}{2} \times
\]

\[
[\text{det}(A^{lk} + B^{lk}; i, j)]^{-\frac{3}{2}} \frac{2\pi \frac{3}{2}}{D'(i,j)[D'(i) + D'(j) + 2b_{ij}^{(N-2)}]^{\frac{1}{2}}},
\]

(4.33)

where the determinant \( \text{det}(A^{lk} + B^{lk}; i, j) \) does not contain columns and rows with indexes \( i \) and \( j \), respectively. Before evaluating the derivatives of the two-body Coulomb integral, let us summarize how this integral was obtained. We demonstrated previously, Chapter II, that this integral results from integration, which we called ‘reduction’, over all coordinates except \( i \) and \( j \). The way of reduction is independent on the order of integration and the quantity \( b_{nm}^{(N-2)} \) can be obtained from a recurrence relation. Let indices \( p_1, p_2, \ldots, p_{N-2} \) denote the consecutive reduction steps (or particles whose coordinates are integrated over in the consecutive reductions) and let \( p_1 \) be the index for the first reduction step, then

\[
b_{nm}^{(1)} = b_{nm}^{(0)} - \frac{1}{a_{p_1} + b_{pp_1}} b_{np_1}^{(0)} b_{mp_1}^{(0)},
\]

(4.34)

is the result of the first reduction, where \( b_{nm}^{(0)} = b_{nm} \). After \( N - 2 \) steps we have

\[
b_{nm}^{(N-2)} = b_{nm}^{(N-3)} - \frac{\text{det}(A^{lk} + B^{lk}; i, j, p_{N-2})}{\text{det}(A^{lk} + B^{lk}; i, j)} b_{np_{N-2}}^{(N-3)} b_{mp_{N-2}}^{(N-3)}.
\]

(4.35)

Additionally, we used the following notation in the expression for the two-body Coulomb integral:

\[
D'(i) = a_{ii}^{lk} + b_{ii}^{(N-2)}; \quad \quad D'(j) = a_{jj}^{lk} + b_{jj}^{(N-2)},
\]

and

\[
D'(i,j) = \begin{bmatrix}
  a_{ii}^{lk} + b_{ii}^{(N-2)} & b_{ij}^{(N-2)} \\
  b_{ij}^{(N-2)} & a_{jj}^{lk} + b_{jj}^{(N-2)}
\end{bmatrix}.
\]

(4.36)
The first derivative with respect to $\xi$ can now be calculated as:

$$
\frac{\partial}{\partial \xi} \ln \left( \omega_i(r_1, r_2, ..., r_N) \bigg| \frac{1}{|r_i - r_j|} \right \omega_k(r_1, r_2, ..., r_N) =

- \langle \omega_i \rangle \frac{1}{|r_i - r_j|} \omega_k \left( \frac{3}{2} \frac{1}{\det(A^{lk} + B^{lk}; i, j)} \left[ \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk}; i, j) \right]

+ \frac{1}{D'(i, j)} \frac{\partial}{\partial \xi} D'(i, j)

+ \frac{1}{2} \left[ D'(i) + D'(j) + 2b_{ij}^{(N-2)} \right] \frac{\partial}{\partial \xi} \left( D'(i) + D'(j) + 2b_{ij}^{(N-2)} \right) \right).

(4.37)

The derivative of $\det(A^{lk} + B^{lk}; i, j)$ can be obtained similarly as was done previously. According to our notation, the above determinant is

$$
det(A^{lk} + B^{lk}; i, j) = det(A^{lk} + B^{lk}|1_{ii}, 1_{jj}),

(4.38)

and when

a) $\xi = \alpha_i^k$;

$$
\frac{\partial}{\partial \alpha_i^k} (1 + \delta_{lk}) det(A^{lk} + B^{lk}|1_{ii}, 1_{jj})

= det(A^{lk} + B^{lk}|1_{ii}, 1_{jj}, 1_{pp})(1 - \delta_{ip})(1 - \delta_{jp})

b) $\xi = \beta_{pq}^k$;

$$
\frac{\partial}{\partial \beta_{pq}^k} det(A^{lk} + B^{lk}|1_{ii}, 1_{jj})

= (1 + \delta_{lk})[det(A^{lk} + B^{lk}|1_{ii}, 1_{jj}, 1_{pp})(1 - \delta_{ip})(1 - \delta_{jp})

+ det(A^{lk} + B^{lk}|1_{ii}, 1_{jj}, 1_{qq})(1 - \delta_{iq})(1 - \delta_{jq})

- 2det(A^{lk} + B^{lk}|1_{ii}, 1_{jj}, 1_{pq})(1 - \delta_{ip})(1 - \delta_{iq})(1 - \delta_{jp})(1 - \delta_{jq})].

Derivatives of $D'(i)$, $D'(j)$ and $D'(i, j)$, i.e.,

$$
\frac{\partial}{\partial \alpha_i^k} D'(i) = (1 + \delta_{lk})\delta_{pi} + \frac{\partial b_{ii}^{(N-2)}}{\partial \alpha_p^k};
\frac{\partial}{\partial \beta_{pq}^k} D'(i) = \frac{\partial b_{ii}^{(N-2)}}{\partial \beta_{pq}^k},

\frac{\partial}{\partial \alpha_i^k} D'(j) = (1 + \delta_{lk})\delta_{pj} + \frac{\partial b_{jj}^{(N-2)}}{\partial \alpha_p^k};
\frac{\partial}{\partial \beta_{pq}^k} D'(j) = \frac{\partial b_{jj}^{(N-2)}}{\partial \beta_{pq}^k},

\frac{\partial}{\partial \alpha_i^k} D'(i, j) = (1 + \delta_{lk})\delta_{pi} + (1 + \delta_{lk})\delta_{pj} + \frac{\partial b_{ij}^{(N-2)}}{\partial \alpha_p^k};
\frac{\partial}{\partial \beta_{pq}^k} D'(i, j) = \frac{\partial b_{ij}^{(N-2)}}{\partial \beta_{pq}^k}.\]
\[
\frac{\partial}{\partial \alpha_p} D'(i, j) = \left( \frac{\partial D'(i)}{\partial \alpha_p} \right) D'(j) + D'(i) \left( \frac{\partial D'(j)}{\partial \alpha_p} \right) - 2 b_{ij}^{(N-2)} \frac{\partial b_{ij}^{(N-2)}}{\partial \alpha_p},
\]
\[
\frac{\partial}{\partial \beta_{pq}} D'(i, j) = \left( \frac{\partial D'(i)}{\partial \beta_{pq}} \right) D'(j) + D'(i) \left( \frac{\partial D'(j)}{\partial \beta_{pq}} \right) - 2 b_{ij}^{(N-2)} \frac{\partial b_{ij}^{(N-2)}}{\partial \beta_{pq}},
\] (4.39)

can be found as the derivative of \( b_{nm}^{(N-2)} \)
\[
\frac{\partial}{\partial \xi} b_{nm}^{(N-2)} = \frac{\partial}{\partial \xi} b_{nm}^{(N-3)}
\]
\[
- \frac{1}{[\det(A^{lk} + B^{lk}; i, j)]^2} \left( \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk}; i, j) \right) \det(A^{lk} + B^{lk}; i, j)
\]
\[
- \det(A^{lk} + B^{lk}; i, j, p) \left( \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk}; i, j, p) \right) b_{np}^{(N-3)} b_{mp}^{(N-3)}
\]
\[
- \frac{\det(A^{lk} + B^{lk}; i, j, p)}{\det(A^{lk} + B^{lk}; i, j)} \left( \frac{\partial b_{np}^{(N-3)}}{\partial \xi} b_{mp}^{(N-3)} + b_{np}^{(N-3)} \frac{\partial b_{mp}^{(N-3)}}{\partial \xi} \right).
\] (4.40)

### 4.3 COMPUTATIONAL IMPLEMENTATION

The procedure for variational calculations based on an effective method for generating nonadiabatic many-particle wave functions with analytical gradients has been computationally implemented. To demonstrate our methodology, let us consider the hydrogen molecule in the ground state. The nonadiabatic four-particle wave function was already presented in Chapter III, Eq.(3.21) and discussed in details. For convenience let us consider only the spatial part
\[
\omega_k = \exp \left[ -(r_A, r_B, r_1, r_2)(A^k + B^k)(r_A, r_B, r_1, r_2)^T \right],
\] (4.41)

where the matrix \((A^k + B^k)\) contains four orbital exponents in the diagonal positions and six correlation exponents, which are subject to optimization. One can restrict both orbital and correlation parameters to be positively definite and perform optimization with constraints. However, such a restriction is unnecessary, though one needs to insist that each basis function, \( \omega_k \), is square-integrable. This can be
accomplished even if some of the exponents are negative. According to the formula for the overlap integral, one has

$$\langle \omega_k | \omega_k \rangle = \frac{2^n}{n!} \left[ \det(A^{kk} + B^{kk}) \right]^{-\frac{1}{2}}, \quad (4.42)$$

which requires that

$$\det(A^{kk} + B^{kk}) > 0 \quad (4.45)$$

for the integral to produce a finite value. This condition is imposed on the nonlinear parameters of each basis function during the optimization.

The expressions derived for the first derivatives of the multiparticle integrals with respect to the non-linear parameters of the Gaussian basis function were computationally implemented and verified vs. the values obtained using the finite difference procedure for differentiation. Next, the derivatives of the Hamiltonian matrix elements, the total energy and the variational functional were assembled and again checked vs. the finite difference results.

In our calculations we used the variable metric method, which is one of the best unconstrained optimization techniques making use of the first derivative. For a given starting point $X_c$, the search vector is computed according to the formula

$$d = -D^{-1}g_c, \quad (4.43)$$

where $D$ is a positive definite approximation of the Hessian, (in the first iteration $D$ is assumed as a unit matrix), and $g_c$ is the gradient evaluated at $X_c$. A line search is then performed to find a new point

$$X_n = X_c + \lambda d, \quad \lambda \in (0, 1], \quad (4.47)$$

such that the values of the functional decreases $g_c$ is used to update $D$ according to the Broyden-Fletcher-Goldfarb-Shanno (BFGS) formula, and another search direction at $X_n$ is then computed to begin the next iteration. According to the formula (4.46), the new search may lead to a situation where condition (4.44) is not fulfilled. One way to resolve this difficulty is to artificially raise the value of the functional when this happens. The second possibility, which is more effective when a long
expansion is used, is to check the normalization condition for each basis function
before the energy evaluation. In the case when a function becomes unnormalized,
the changes of the nonlinear parameters for this function are reduced.

4.4 NUMERICAL EXAMPLE

The calculations we did to illustrate the performance of the gradient-based
optimization technique of the non-adiabatic wave function, developed in the present
study pertain to the ground state of the $H_2$ molecule. The most interesting results
of the calculations are the nonadiabatic four-particle wave functions obtained for
different values of $k$ as well as the corresponding total energies and the magnitude
of the kinetic energy of the CM motion. We used five Gaussian cluster functions in

| TABLE V. Ground state energies computed with different $k$
values for the $H_2$ molecule. |
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>Method I</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>Method II</td>
</tr>
<tr>
<td>-1</td>
</tr>
</tbody>
</table>

$a)$ see footnote in TABLE I.
the expansion. First we performed optimization of the functional (3.5) using Method I. All 50 parameters, i.e., orbital and correlation exponents, have been optimized with the procedure described in the previous section. Then we performed optimization of the functional without the penalty term, i.e., with $k$ equal to zero. Next, we used the optimal set of parameters as a starting point for optimization with $k = 100$. The values of the functional $J[\Psi_{\text{TOT}}; k]$, the total energy $E$ and the energy of the CM motion are given in Table V. Since we used a short expansion, the experimental energy of the $H_2$ molecule is rather poorly reproduced, nevertheless, the calculations allow us to demonstrate the characteristic features of the Gaussian cluster basis sets resulting from optimizations with different $k$ values. When the parameter $k$ is equal to zero, the value of the functional is equal to the value of the total energy. The value of the kinetic energy of CM motion is of order $10^{-7}$. When the penalty term is increased by setting $k = 100$, the optimization is noticeably more focused on minimizing the kinetic energy of the CM motion. The value of the variational functional becomes higher as well as the total energy in comparison to the case with $k = 0$. The main difference is the energy of the CM motion $T_{\text{CM}}$, which decreases by two orders of magnitude. This value can be reduced even further by using a larger value of $k$. To illustrate the performance of the procedure, we show in FIG. 1 how the value of $T_{\text{CM}}$ changes during the optimization. We eliminated the points for which the value of the functional is higher than the actual minimum. Upon examining the curves, one notices that for $k = 100$ the energy of the CM motion was much more effectively suppressed than in the optimization without the penalty term.

The second result which we would like to demonstrate is the Gaussian cluster basis functions obtained from optimizations with $k = -1$, $k = 0$ and $k = 100$. Results are summarized in Tables VI, VII and VIII. Let us focus on the values of orbital parameters, $\alpha_A^k$, $\alpha_B^k$, $\alpha_1^k$ and $\alpha_2^k$. Upon examining the values of these parameters for $k = -1$, one notices that the nuclear parameters are larger than electronic parameters and very similar in all basis functions indicating some localization of the protons around the center of the coordinate system. For $k = 0$ (Table VII), all nuclear orbital parameters become much smaller. This is expected because for smaller orbital exponents the system becomes more delocalized around the center
of the coordinate system and this leads to a lower kinetic energy of the CM motion which is now present in the variational function. The orbital parameters for the electrons are one or two orders of magnitude smaller than the orbital parameters for the protons for each function used in the expansion. This reflects the fact that electrons are more weakly 'attached' to the origin of the coordinate system than protons. However, electrons must be bonded to the protons through the correlation factors so they do not escape to infinity. The values of the orbital exponents for \( k = 100 \) become even smaller, i.e., more diffused. For the correlation exponents, there are no significant differences between the two cases.
FIG. 1. The change of the value of $T_{CM}$ during the optimization procedure. Points corresponding to functional values higher than the actual minimum were eliminated.
TABLE VI. Optimized orbital and correlation exponents for the $H_2$ molecule with $k = -1$.

<table>
<thead>
<tr>
<th>Orbital exponent</th>
<th>Numerical value</th>
<th>Correlation exponent</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1^A$</td>
<td>0.10790982</td>
<td>$\beta_{A1}^1$</td>
<td>2.84911836×10^{-2}</td>
</tr>
<tr>
<td>$\alpha_1^B$</td>
<td>0.10428127</td>
<td>$\beta_{A1}^1$</td>
<td>4.50685317×10^{-2}</td>
</tr>
<tr>
<td>$\alpha_1^1$</td>
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<td>$\beta_{A1}^2$</td>
<td>0.26552975</td>
</tr>
<tr>
<td>$\alpha_2^A$</td>
<td>1.36097725×10^{-5}</td>
<td>$\beta_{B1}^2$</td>
<td>0.73127272</td>
</tr>
<tr>
<td>$\alpha_2^B$</td>
<td>1.36097725×10^{-5}</td>
<td>$\beta_{B2}^2$</td>
<td>5.51001819×10^{-3}</td>
</tr>
<tr>
<td>$\alpha_2^1$</td>
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<td>$\beta_{B2}^1$</td>
<td>-1.56974348×10^{-2}</td>
</tr>
<tr>
<td>$\alpha_2^2$</td>
<td>0.73127272</td>
<td>$\beta_{B2}^1$</td>
<td>-1.56974348×10^{-2}</td>
</tr>
<tr>
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<td>$\beta_{A2}^2$</td>
<td>5.48039000×10^{-2}</td>
</tr>
<tr>
<td>$\alpha_3^B$</td>
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<td>$\beta_{A2}^2$</td>
<td>2.10794188×10^{-2}</td>
</tr>
<tr>
<td>$\alpha_3^1$</td>
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<td>$\beta_{A2}^2$</td>
<td>0.14952032</td>
</tr>
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</tr>
<tr>
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<td>$\beta_{B2}^2$</td>
<td>8.05877124×10^{-3}</td>
</tr>
<tr>
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<td>$\beta_{B2}^2$</td>
<td>2.39329290×10^{-2}</td>
</tr>
<tr>
<td>$\alpha_4^A$</td>
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<td>$\beta_{A1}^3$</td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>$\alpha_4^4$</td>
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<td>$\alpha_5^2$</td>
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<td>0.29258723</td>
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<td>$\beta_{A1}^4$</td>
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<td>$\beta_{A1}^4$</td>
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TABLE VII. Optimized orbital and correlation exponents for the $H_2$ molecule with $k = 0$.

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<th>Numerical value</th>
<th>Correlation exponent</th>
<th>Numerical value</th>
</tr>
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<tbody>
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<td>$\beta_{AB}$</td>
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<tr>
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<td>$1.08228801$</td>
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<tr>
<td></td>
<td></td>
<td>$\beta_{B2}$</td>
<td>$5.90706590 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
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<td>$\beta_{AB}$</td>
<td>$0.13748912$</td>
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<td>$\alpha_2^B$</td>
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<td>$\beta_{A1}$</td>
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<td></td>
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</tr>
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</table>
TABLE VIII. Optimized orbital and correlation exponents for the $H_2$ molecule with $k = 100$.

<table>
<thead>
<tr>
<th>Orbital exponent</th>
<th>Numerical value</th>
<th>Correlation exponent</th>
<th>Numerical value</th>
</tr>
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<tr>
<td>$\alpha_{A1}^1$</td>
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4.5 CONCLUSIONS

The subject of this Chapter was to demonstrate nonadiabatic calculations utilizing our previously proposed method, outlined in Chapter III, combined with the analytical derivative technique. As mentioned before, this method does not require a rigorous separation of the CM motion by transformation to an appropriate set of internal coordinates. Instead, the value of the kinetic energy of the CM motion is subtracted from the variational function (Method I), or effectively reduced via a penalty term introduced to the variational functional (Method II). In the present study we utilized analytical first derivatives of the variational functional with respect to nonlinear parameters appearing in the Gaussian cluster basis functions. The analytical derivatives have been derived and implemented. The methodology presented here can easily be extended to systems with more particles, which is rather difficult to achieve with the use of conventional approaches.
CHAPTER V
NEWTON-RAPHSON METHOD

5.1 INTRODUCTION

During the last two decades the theory of analytical derivatives has received much attention in quantum chemistry. Analytical derivative theory involves calculation of derivatives of the Born-Oppenheimer potential energy with respect to the nuclear coordinates. Analytical derivatives have also been used for calculations of electric and magnetic properties (energy derivatives with respect to applied external field) as well as derivatives of the energy leading to evaluation of forces and force constants. Since the early works of Pulay [89,90], analytical derivatives have been obtained for the self-consistent-field theory and beyond [91]. The first and second derivatives are well known for most of the \textit{ab-initio} quantum-chemical methods [92-94], and are commonly used in quantum mechanical calculations [95]. Higher analytical derivatives, \textit{i.e.} third and fourth, have been recently obtained by Handy and co-workers [96,97] and have been used in conjunction with the anharmonic spectroscopic properties. Another application of the analytical derivatives has been in the optimization of exponents of Gaussian-type atomic orbitals.

The subject of this Chapter is to demonstrate the application of the second derivatives for optimization of the exponents of explicitly correlated Gaussian-type functions. The presented algorithms are general and can be applied to different problems including electronic structure calculations where the explicitly correlated Gaussian-type functions have been employed in the past with a great deal of success [50-74]. In this Chapter we use the analytical derivative technique in conjunction with the Newton-Raphson optimization procedure for generating the nonadiabatic
wave function with the method proposed in previous Chapters. In this approach the motion of all particles (electrons and nuclei) are considered at the same time. The elimination of the CM motion is achieved by introducing an additional term to the variational functional representing the kinetic energy of the center-of-mass motion. First we will demonstrate the algorithm for calculation of the first and second derivatives of the variational functional with respect to the Gaussian exponents. Next, the computational implementation is discussed and some numerical examples are presented.

5.2 PRELIMINARES

The general form of an \(N\)-particle many-body nonadiabatic wave function, which has been subject of the previous Chapters, has the following form

\[
\Psi = \sum_{k=1}^{M} c_k P(1, 2, \ldots, N)[\omega_k(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Theta_{S,M}^N],
\]  

(5.1)

where \(\omega_k\) and \(\Theta_{S,M}^N\) represent the spatial and spin components, respectively. The spatial component is the following Gaussian cluster function

\[
\omega_k = \exp \left( -\sum_{i=1}^{N} \alpha_i^k |\mathbf{r}_i - \mathbf{R}_i^k|^2 - \sum_{i=1}^{N} \sum_{j>i}^{N} \beta_{ij}^k |\mathbf{r}_i - \mathbf{r}_j|^2 \right).
\]  

(5.2)

In our previous Chapters we proposed an effective variational approach to generate the expansion Eq.(5.1). One can expect that, evaluating the total energy of the system as

\[
E = \frac{\langle \Psi | H_{TOT} | \Psi \rangle}{\langle \Psi | \Psi \rangle},
\]  

(5.3)

where

\[
H_{TOT} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{r_{ij}},
\]  

(5.4)

with the wave function (5.1), the contribution from the kinetic energy of the motion of the CM will be present in the total energy. In order to eliminate this contribution
we proposed two methods (Method I and Method II) where the following variational functional has been utilized

$$J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] = \frac{\langle \Psi | H_{TOT} | \Psi \rangle + k \langle \Psi | T_{CM} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (5.5)$$

where $k$ is a constant scaling the positive term that represents the kinetic energy of the motion of the center-of-mass. In the first method we used a large positive value of $k$, which led to a significant reduction of the magnitude of the $\langle \Psi | T_{CM} | \Psi \rangle$ term in the optimization process. The optimal variational wave function was subsequently used to calculate the total energy of the system with the use of Eq.(5.3). Since the contribution of the CM motion in this energy was negligible, the obtained value was identified as the internal energy of the system. In the second method we set $k$ equal to $-1$. As a consequence, the variational functional (5.5) represented only the internal energy of the system since

$$J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; -1] = \frac{\langle \Psi | H_{TOT} | \Psi \rangle - \langle \Psi | T_{CM} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Psi | H_{\text{int}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (5.6)$$

and its optimized value provided an upper bound to the internal energy. In previous Chapter we concluded based on some numerical evidence that both methods produce similar results mainly dependent on the length of the expansion of the wave function. However, for the same expansion length, the second method seemed to perform better and converge faster.

The problem which arises in minimization of the variational functional (5.5) is the number of nonlinear parameters in the wave function which should be optimized. This number increases very rapidly with the length of the expansion and the optimization procedure becomes very expensive.

Let $X(x_1, x_2, ..., x_n)$ be the n-dimensional vector of nonlinear parameters, i.e., both orbital and correlation exponents. The Taylor expansion of the functional about point $X^*$ can be obtained as follows

$$J[X; k] = J[X^*; k] + \sum_{i=1}^{n} \left. \frac{\partial J[X; k]}{\partial x_i} \right|_{X^*} (x_i - x_i^*) +$$

$$\frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left. \frac{\partial^2 J[X; k]}{\partial x_i \partial x_j} \right|_{X^*} (x_i - x_i^*)(x_j - x_j^*) + ... \quad (5.7)$$
or, in the matrix form (the expansion is truncated after the quadratic term)

\[ J[X; k] = \]

\[ J[X^*; k] + \nabla J[X; k]\bigg|_X^T (X - X^*) + \frac{1}{2} (X - X^*)^T H_{X^*} (X - X^*), \quad (5.8) \]

where \( H_{X^*} \) denotes the Hessian evaluated at the \( X^* \) point. At a minimum the gradient becomes equal to zero, \( \nabla J[X; k]\big|_X^T = 0 \). If the expansion (5.8) is dominated by the linear and quadratic term and the Hessian matrix is positive defined, then one can use the approximate quadratic expression to find the minimum of the functional:

\[ X_{MIN} = -H(X)_{X^*}^{-1} (\nabla J[X; k]\big|_X^T). \quad (5.9) \]

Let us consider the first and second derivatives of the functional \( J[\{\alpha_p\}, \{\beta_{pq}\}; k] \) with respect to an arbitrary parameter \( \xi \),

\[ \frac{\partial}{\partial \xi} J[\{\alpha_p\}, \{\beta_{pq}\}; k] = \frac{1}{\langle \Psi | \Psi \rangle} \left[ \frac{\partial}{\partial \xi} (\langle \Psi | H | \Psi \rangle + k \frac{\partial}{\partial \xi} (\langle \Psi | TCM | \Psi \rangle) \right] \]

\[ - J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] \frac{1}{\langle \Psi | \Psi \rangle} \frac{\partial}{\partial \xi} (\langle \Psi | \Psi \rangle). \quad (5.10) \]

where \( \xi \) can be \( \alpha_p^i \) or \( \beta_{pq}^i \). The second derivative of energy with respect to \( \xi \) and \( \zeta \) can be obtained in similar way

\[ \frac{\partial^2}{\partial \xi \partial \zeta} J[\{\alpha_p\}, \{\beta_{pq}\}; k] = \frac{1}{\langle \Psi | \Psi \rangle} \left[ \frac{\partial^2}{\partial \zeta \partial \xi} (\langle \Psi | H | \Psi \rangle + k \frac{\partial}{\partial \zeta} (\langle \Psi | TCM | \Psi \rangle) \right] \]

\[ - \frac{1}{\langle \Psi | \Psi \rangle} \left( \frac{\partial}{\partial \zeta} (\langle \Psi | \Psi \rangle) \right) \left( \frac{\partial}{\partial \xi} J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] \right) \]

\[ - \frac{1}{\langle \Psi | \Psi \rangle} \left( \frac{\partial}{\partial \zeta} (\langle \Psi | \Psi \rangle) \right) \left( \frac{\partial}{\partial \xi} J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] \right) \]

\[ - J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] \frac{1}{\langle \Psi | \Psi \rangle} \frac{\partial^2}{\partial \zeta \partial \xi} (\langle \Psi | \Psi \rangle). \quad (5.11) \]

As it was mention previously the set of linear coefficients is obtained by solving the secular equation. In the case of the Method I, this set is not optimal with respect to the variational functional \( J \), because \( J \) contains additional term \( k \langle \Psi | TCM | \Psi \rangle \) which
is not present in the secular equation. However, the set becomes optimal if \( k \) is equal to zero, or when the kinetic energy of the center of mass motion vanishes. Therefore, the smaller the \( \langle \Psi |T_{CM}|\Psi \rangle \) term is, the more fulfilled the condition

\[
\frac{\partial}{\partial c_i} J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] = 0
\]  

(5.12)

should become. In Method II the solution of the secular equation implies that the above equation is exactly satisfied at each step of the minimization process. To make Eqs (5.10) and (5.11) more explicit let us consider a matrix element with the function given by Eq.(5.1)

\[
\langle \Psi |\hat{O}|\Psi \rangle = \sum_{l=1}^{M} \sum_{k=1}^{M} c_{l} c_{k} \langle P[\omega_l |\Theta^N_{S,M}]|\hat{O}|\omega_k |\Theta^N_{S,M}\rangle,
\]  

(5.13)

where \( \hat{O} = H_{TOT}, T_{CM} \) or 1. The derivative with respect to \( \xi^k \) is

\[
\frac{\partial}{\partial \xi^k} \langle \Psi |\hat{O}|\Psi \rangle = \sum_{l=1}^{M} (1 + \delta_{lk}) c_{l} c_{k} \langle P[\omega_l |\Theta^N_{S,M}]|\hat{O}|\omega_k |\Theta^N_{S,M}\rangle \frac{\partial}{\partial \xi^k} \omega_k |\Theta^N_{S,M}\rangle,
\]  

(5.14)

where the derivative of the above matrix element was consider with a fixed linear coefficient, since we did not consider derivatives of linear coefficients with respect to Gaussian exponents. The second derivative with respect to \( \xi^l \) when \( l \neq k \) is

\[
\frac{\partial^2}{\partial \xi^i \partial \xi^k} \langle \Psi |\hat{O}|\Psi \rangle = (1 + \delta_{lk}) c_{l} c_{k} \langle P[\omega_l |\Theta^N_{S,M}]|\hat{O}|\omega_k |\Theta^N_{S,M}\rangle \frac{\partial^2}{\partial \xi^k \partial \xi^l} \omega_k |\Theta^N_{S,M}\rangle,
\]  

(5.15a)

while

\[
\frac{\partial^2}{\partial \xi^l \partial \xi^k} \langle \Psi |\hat{O}|\Psi \rangle = (1 + \delta_{lk}) c_{l} c_{k} \langle P[\omega_l |\Theta^N_{S,M}]|\hat{O}|\omega_k |\Theta^N_{S,M}\rangle \frac{\partial^2}{\partial \xi^k \partial \xi^l} \omega_k |\Theta^N_{S,M}\rangle,
\]  

(5.15b)

In the present study, we only consider the case where all orbital centers \( R_i^k \) coincide with the center of the coordinate system. By introducing the diagonal matrix, \( A^k \), of the orbital exponents, the expression for \( \omega_k \) becomes

\[
\omega_k = \exp \left[ -r(A^k + B^k)r^T \right],
\]  

(5.16)
and all required integrals can be expressed in terms of the \((A^k + B^k)\) matrix elements.

Before we demonstrate evaluation of the second derivatives of the integrals, for clarity of the presentation, let us summarize some results presented in the previous paper pertaining to the theory of the first derivative. Let us first consider the determinant of the \((A^k + B^k)\) matrix and its derivative with respect to the nonlinear parameters. The derivative with respect to the orbital exponent, \(\alpha^k_p\), is achieved by setting the \(p'\)th column and the \(p'\)th row equal to zero, and the \((A^k + B^k)_{p,p'}\) element equal to 1. In our previous notation this operation was denoted as

\[
\frac{\partial}{\partial \alpha^k_p} \det(A^k + B^k) = \det(A^k + B^k|_{1_{pp}}).
\]  

(5.17)

Determination of the second derivatives requires differentiation of the same determinate twice with respect to two nonlinear parameters. For clarity of the presentation, let us introduce a more compact notation of the result of the differentiation of determinate \(\det(A^k + B^k)\), namely

\[
\frac{\partial}{\partial \alpha^k_p} \det(A^k + B^k) = D^k(p_p).
\]  

(5.18)

Before we consider the derivative with respect to \(\beta^k_{pq}\) let us differentiate \(\det(A^k + B^k)\) with respect to the diagonal and off-diagonal elements of the \(B^k\) matrix. The differentiation with respect to \(b^k_{pp}\), appearing in the \(pp\) diagonal element, is carried out in a similar way as for \(\alpha^k_p\). For the off-diagonal elements one needs to multiply the expression by a factor of 2,

\[
\frac{\partial}{\partial b^k_{pq}} \det(A^k + B^k) = (2 - \delta_{pq}) D^k(p_q).
\]  

(5.19)

The last required differentiation, with respect to \(\beta^k_{pq}\), can be transformed to differentiation with respect to \(b^k_{pq}\) using the chain rule

\[
\frac{\partial}{\partial \beta^k_{pq}} = \left( \frac{\partial b^k_{pp}}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b^k_{pp}} + \left( \frac{\partial b^k_{pq}}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b^k_{pq}} + \left( \frac{\partial b^k_{qp}}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b^k_{qp}} + \left( \frac{\partial b^k_{qq}}{\partial \beta^k_{pq}} \right) \frac{\partial}{\partial b^k_{qq}}.
\]  

(5.20)
For $\beta^k_{pq}$, subscript $p$ is always different than $q$.

Let us now consider derivatives with respect to $\alpha^k_p$ and $\beta^k_{pq}$ of the $(A^{lk} + B^{lk})$ determinant, where $A^{lk}$ denotes $A^t + A^k$, and $B^{lk}$ denotes $B^t + B^k$. Upon examining the structure of the matrix $B^{lk}$ one obtains

$$\frac{\partial b_{ij}^{lk}}{\partial \beta^k_{pq}} = (1 + \delta_{ik}) \Delta(i, j; p, q), \quad (5.21)$$

where

$$\Delta(i, j; p, q) = \delta_{ij}(\delta_{ip} + \delta_{jq}) - (\delta_{ip}\delta_{jq} + \delta_{iq}\delta_{jp}). \quad (5.22)$$

Using the above relation, Eq.(5.20) simplifies to

$$\frac{\partial}{\partial \beta^k_{pq}} = (1 + \delta_{lk}) \left[ \frac{\partial}{\partial b_{pp}^{lk}} + \frac{\partial}{\partial b_{qq}^{lk}} - \frac{\partial}{\partial b_{pq}^{lk}} - \frac{\partial}{\partial b_{qp}^{lk}} \right], \quad (5.23)$$

and differentiation with respect to $\beta^k_{pq}$ can be easily evaluated

$$\frac{\partial}{\partial \beta^k_{pq}} det(A^{lk} + B^{lk}) = (1 + \delta_{lk}) [D^{lk}(\nu_p) + D^{lk}(\nu_q) - 2D^{lk}(\nu_p)] \quad (5.24)$$

because the matrix $(A^{lk} + B^{lk})$ is symmetric. Similarly,

$$\frac{\partial}{\partial \alpha^k_p} det(A^{lk} + B^{lk}) = (1 + \delta_{lk}) D^{lk}(\nu_p) . \quad (5.25)$$

Now, let us consider double differentiation of the determinant with respect to two nonlinear parameters. For the double differentiation of $det(A^{lk} + B^{lk})$ with respect to two orbital exponents one obtains

$$\frac{\partial^2}{\partial \alpha^k_p \partial \alpha^k_p} det(A^{lk} + B^{lk}) = (1 + \delta_{lk}) \frac{\partial}{\partial \alpha^k_p} det(A^{lk} + B^{lk}|_{\nu_p}) . \quad (5.26)$$

Using the Laplace expansion it can be demonstrated that the result of differentiation is equal to

$$\frac{\partial^2}{\partial \alpha^k_p \partial \alpha^k_p} det(A^{lk} + B^{lk}) = (1 - \delta_{pq})(1 + \delta_{lk})^2 det(A^{lk} + B^{lk}|_{\nu_p, \nu_q}) . \quad (5.27)$$

This result is particularly important from a computational point of view. A double differentiation is equivalent to setting the appropriate columns and rows equal to
zero and the elements with subscripts $pp$ and $qq$ equal to $(1 + \delta_{ik})$ in the matrix $(A^{lk} + B^{lk})$. In the case when $q = p$ the result of differentiation is equal to zero. Hence, the factor $(1 - \delta_{pq})$ was introduced. Similarly, a double differentiation with respect to $\beta_{pq}^k$ and $\alpha_{p'}^l$, results in

$$\frac{\partial^2}{\partial \alpha_{p'}^l \partial \beta_{pq}^k} \det(A^{lk} + B^{lk}) = (1 + \delta_{lk})^2 \times$$

$$[\det(A^{lk} + B^{lk}|_{1_{pp'1_{p'q'}}})(1 - \delta_{pp'})$$

$$+ \det(A^{lk} + B^{lk}|_{1_{qq'1_{p'p'}}})(1 - \delta_{qq'})$$

$$- \det(A^{lk} + B^{lk}|_{1_{pq'1_{p'p'}}})(1 - \delta_{pp'})(1 - \delta_{qq'})$$

$$- \det(A^{lk} + B^{lk}|_{1_{qp'1_{p'p'}}})(1 - \delta_{pp'})(1 - \delta_{qq'})].$$

(5.28)

where we used our previously introduced notation. To make the last formula more compact let us extend the notation given by Eqs (5.24) and (5.25) in the following way

$$D_{lk}^{p',q'}(p,p') = \det(A^{lk} + B^{lk}|_{1_{pq'1_{p'p'}}})(1 - \delta_{pp'})(1 - \delta_{q,q'}).$$

(5.29)

Now, Eq.(5.28) can be rewritten as

$$\frac{\partial^2}{\partial \alpha_{p'}^l \partial \beta_{pq}^k} \det(A^{lk} + B^{lk}) =$$

$$(1 + \delta_{lk})^2 \left[D_{lk}^{p',q'}(p,p') + D_{lk}^{p,q'}(p,p') - D_{lk}^{p',q'}(p,p') - D_{lk}^{p,q'}(p,p') \right].$$

(5.30)

For both parameters being correlation exponents, $\zeta = \beta_{pq}^k$ and $\xi = \alpha_{p'}^l$, the second derivative reads

$$\frac{\partial^2}{\partial \beta_{p'q'}^l \partial \beta_{pq}^k} \det(A^{lk} + B^{lk}) =$$

$$(1 + \delta_{lk})^2 \left[D_{lk}^{p',q'}(p,p') + D_{lk}^{p,q'}(p,p') - D_{lk}^{p',q'}(p,p') - D_{lk}^{p,q'}(p,p') \right]$$

$$+ D_{lk}^{p',q'}(q,q') + D_{lk}^{p,q'}(q,q') - D_{lk}^{p',q'}(q,q') - D_{lk}^{p,q'}(q,q')$$

$$- D_{lk}^{p',q'}(q,q') + D_{lk}^{p,q'}(q,q') + D_{lk}^{p,q'}(q,q').$$
\[
-D^{lk}_{pp'}(q,p') - D^{lk}_{pq'}(q,q') + D^{lk}_{pq'}(q,p') + D^{lk}_{pp'}(q,q')
\]  
(5.31)

The above notation can be extended for an arbitrary number of differentiations without any ambiguity. As an example let us consider the quantity \( D^{lk}_{pp',s} \). The factor which contains the Kronecker delta is generated by considering all possible pairs from the set \( \{p, p', s\} \), and from the set \( \{p, p', s\} \). Each pair gives rise to a factor involving a Kronecker delta \( \delta_{p,p'} \), \( \delta_{p,s} \), \( \delta_{p',s} \), \( \delta_{p',r} \). The product of these two gives the total factor, \( \delta_{p,p'}(1-\delta_{p,s})(1-\delta_{p',s}) \). This factor multiplies the determinant of the \( (A^{lk} + B^{lk}) \) matrix in which \( pp, p'p' \) and \( sr \) elements were set to one and in which \( p, p' \) and \( s \) rows were set to zero as well as \( p, p' \) and \( r \) columns. The above scheme makes the formulas more compact and readable.

5.3 SECOND DERIVATIVES OF MOLECULAR INTEGRALS WITH RESPECT TO GAUSSIAN EXONENTS

In this section we will demonstrate the second derivatives of the one-center multiparticle integrals over explicitly correlated Gaussian functions with respect to the Gaussian exponents. The first derivatives with respect to the orbital exponents and the correlation exponents were derived in the previous Chapter. The second derivatives presented in this section will be expressed in terms of the first derivatives, the derivatives of the determinant \( \text{det}(A^{lk} + B^{lk}) \) and some other simple derivatives. This representation makes the formulas compact and easily programmable. Before we demonstrate the second derivatives of the integrals let us consider the following general matrix element

\[
(\Psi|\hat{O}|\Psi) = I(\alpha_1^l, \ldots, \alpha_N^l, \alpha_{1N}^k, \ldots, \alpha_{NK}^k, \beta_1^l, \ldots, \beta_{NKP}^l, \beta_{1N}^k, \ldots, \beta_{NP}^k).
\]  
(5.32)

where \( NP = N \times (N - 1)/2 \), and \( N \) is the number of particles. Each integral is a function of \( 2 \times (N + NP) \) nonlinear parameters. The second derivatives of the above integral form a square matrix of the dimension \( N + NP \). For all the derivatives one needs to consider three cases: The first one corresponds to the second derivative
with respect to two orbital exponents; the second is the case of a mixed derivative with respect to orbital and correlation exponents; the third is the derivative with respect to two correlation exponents. For some integrals these three categories do not exhaust all the possibilities and some more specific cases need to be considered.

First, let us consider the overlap integral

$$\langle \omega_l(r_1, r_2, \ldots, r_N) | \omega_k(r_1, r_2, \ldots, r_N) \rangle = \pi^{N-1} \left[ \det(A^{lk} + B^{lk}) \right]^{-\frac{3}{2}}. \quad (5.33)$$

As derived in the previous Chapter the first derivative with respect to $\xi$ representing an orbital or correlation exponent is

$$\frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle = -\frac{3}{2} \pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{3}{2}} \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk}). \quad (5.34)$$

The second derivative with respect to $\xi$ and $\zeta$ can be calculated in a similar way as the first derivatives and it becomes

$$\frac{\partial^2}{\partial \zeta \partial \xi} \langle \omega_l | \omega_k \rangle =$$

$$\frac{15}{4} \pi^{-2N} \langle \omega_l | \omega_k \rangle^{\frac{5}{2}} \left[ \frac{\partial}{\partial \zeta} \det(A^{lk} + B^{lk}) \right] \left[ \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk}) \right]$$

$$- \frac{3}{2} \pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{3}{2}} \frac{\partial^2}{\partial \zeta \partial \xi} \det(A^{lk} + B^{lk}). \quad (5.35)$$

Since,

$$\left( \frac{\partial}{\partial \zeta} \langle \omega_l | \omega_k \rangle \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) =$$

$$\frac{9}{4} \pi^{-2N} \langle \omega_l | \omega_k \rangle^{-\frac{1}{2}} \left[ \frac{\partial}{\partial \zeta} \det(A^{lk} + B^{lk}) \right] \left[ \frac{\partial}{\partial \xi} \det(A^{lk} + B^{lk}) \right], \quad (5.36)$$

the derivative can be simplified as

$$\frac{\partial^2}{\partial \zeta \partial \xi} \langle \omega_l | \omega_k \rangle =$$

$$\frac{5}{3} \langle \omega_l | \omega_k \rangle^{-1} \left( \frac{\partial}{\partial \zeta} \langle \omega_l | \omega_k \rangle \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right)$$

$$- \frac{3}{2} \pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{3}{2}} \frac{\partial^2}{\partial \zeta \partial \xi} \det(A^{lk} + B^{lk}). \quad (5.37)$$
The appropriate derivatives of the determinant have been discussed in the previous section.

The kinetic energy integral can be expressed in terms of the following integral,

\[ I_{ij}^{lk} = \iint \ldots \int [\nabla_i \omega_l(r_1, r_2, \ldots r_N)] [\nabla_j \omega_k(r_1, r_2, \ldots r_N)] dr_1 dr_2 \ldots dr_N. \]  

(5.38)

It has been demonstrated previously that \( I_{ij}^{lk} \) has the following form

\[ I_{ij}^{lk} = 4 \sum_{m=1}^{N} \sum_{s=1}^{N} (\alpha_m^l \delta_{mi} + b_{im}^l) (\alpha_s^k \delta_{sj} + b_{js}^k) J(r_m, r_s; 1, 1). \]

(5.39)

for a one center function and \( J(r_p, r_q; n_1, n_2) \) represents the generalized overlap integral

\[ J(r_p, r_q; n_1, n_2) = \int \ldots \int r_p^{n_1} r_q^{n_2} \exp \left( -\sum_{n=1}^{N} a_n^l |r_n - R_n^{lk}|^2 - r B^{lk} r^T \right) dr_1 dr_2 \ldots dr_N. \]

(5.40)

After some algebraic manipulations the expression for \( I_{ij}^{lk} \) becomes

\[ I_{ij}^{lk} = \frac{6 \langle \omega_l | \omega_k \rangle}{\det(A^{lk} + B^{lk})} W_{ij} \]

(5.41)

where

\[ W_{ij} = \sum_{m=1}^{N} \sum_{s=1}^{N} (\alpha_m^l \delta_{mi} + b_{im}^l) (\alpha_s^k \delta_{sj} + b_{js}^k) D^{lk(m)}(n). \]

(5.42)

The second derivative with respect to \( \zeta \) and \( \xi \) can be handled similarly as the derivatives of the overlap integral

\[ \frac{\partial^2}{\partial \zeta \partial \xi} T_{lk} = \frac{1}{2} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \zeta \partial \xi} I_{ij}^{lk}, \]

(5.43)

and similarly for the integral representing the center-of-mass motion

\[ \frac{\partial^2}{\partial \zeta \partial \xi} (T_{CM})_{lk} = \frac{1}{2M} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial^2}{\partial \zeta \partial \xi} I_{ij}^{lk}. \]

(5.44)
As derived in the previous Chapter the first derivative of the kinetic energy integral reads

\[
\frac{\partial}{\partial \xi} T_{lk} = \frac{5}{3} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) + \frac{3 \langle \omega_l | \omega_k \rangle}{\det(A^{lk} + B^{lk})} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial}{\partial \xi} W_{ii}, \tag{5.45}
\]

which together with the expression for the overlap integral can be rearranged to the form

\[
\frac{\partial}{\partial \xi} T_{lk} = \frac{5}{3} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) + 3\pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{5}{3}} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial}{\partial \xi} W_{ii}. \tag{5.46}
\]

The second derivative of the kinetic energy integrals can now be calculated as

\[
\frac{\partial^2}{\partial \zeta \partial \xi} T_{lk} = \frac{5}{3} \frac{1}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \zeta} T_{lk} \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) \\
- \frac{5}{3} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle^2} \left( \frac{\partial}{\partial \zeta} \langle \omega_l | \omega_k \rangle \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) \\
+ \frac{5}{3} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle} \frac{\partial^2}{\partial \zeta \partial \xi} \langle \omega_l | \omega_k \rangle + 5\pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{5}{3}} \left( \frac{\partial}{\partial \zeta} \langle \omega_l | \omega_k \rangle \right) \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial}{\partial \xi} W_{ii} \\
+ 3\pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{5}{3}} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \zeta \partial \xi} W_{ii}. \tag{5.47}
\]

The last expression for the second derivative can be made symmetric with respect to \( \zeta \) and \( \xi \) by using Eq.(5.45)

\[
\frac{\partial^2}{\partial \zeta \partial \xi} T_{lk} = \\
\frac{5}{3} \frac{1}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \zeta} T_{lk} \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) + \frac{5}{3} \frac{1}{\langle \omega_l | \omega_k \rangle} \left( \frac{\partial}{\partial \zeta} T_{lk} \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) \\
+ \frac{5}{3} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle} \frac{\partial^2}{\partial \zeta \partial \xi} \langle \omega_l | \omega_k \rangle - \frac{40}{9} \frac{T_{lk}}{\langle \omega_l | \omega_k \rangle^2} \left( \frac{\partial}{\partial \zeta} \langle \omega_l | \omega_k \rangle \right) \left( \frac{\partial}{\partial \xi} \langle \omega_l | \omega_k \rangle \right) \\
+ 3\pi^{-N} \langle \omega_l | \omega_k \rangle^{\frac{5}{3}} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \zeta \partial \xi} W_{ii}. \tag{5.48}
\]
The expression for the second derivative of the kinetic energy of the CM motion has a similar form, but the matrix element $T_{lk}$ should be replaced by $(T_{CM})_{lk}$ and the last term, i.e., $\sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial \xi^2} W_{ii}$ by $\frac{1}{M} \sum_{j=1}^{N} \sum_{k=1}^{N} \frac{\partial^2}{\partial \xi^2} W_{ij}$.

Most of the terms appearing in the last equation have been evaluated either in previous Chapter, or for the derivatives for the overlap integral. The only element which should be discussed is the second derivative of $W_{ij}$. The general second derivative can be calculated as

$$\frac{\partial^2}{\partial \zeta \partial \xi} W_{ij} = \sum_{m=1}^{N} \sum_{s=1}^{N} \left( \left[ \frac{\partial}{\partial \xi} (\alpha_m^l \delta_{mi} + b_{im}^l) \right] \left[ \frac{\partial}{\partial \zeta} (\alpha_s^k \delta_{sj} + b_{js}^k) \right] D^{lk}(m)_{s} \right)$$

$$+ \left[ \frac{\partial}{\partial \xi} (\alpha_m^l \delta_{mi} + b_{im}^l) \right] \left( \alpha_s^k \delta_{sj} + b_{js}^k \right) \frac{\partial}{\partial \zeta} D^{lk}(m)_{s}$$

$$+ \left[ \frac{\partial}{\partial \zeta} (\alpha_m^l \delta_{mi} + b_{im}^l) \right] \left( \alpha_s^k \delta_{sj} + b_{js}^k \right) \frac{\partial}{\partial \xi} D^{lk}(m)_{s}$$

$$+ \left[ \frac{\partial}{\partial \xi} (\alpha_m^l \delta_{mi} + b_{im}^l) \right] \left( \alpha_s^k \delta_{sj} + b_{js}^k \right) \frac{\partial}{\partial \zeta} D^{lk}(m)_{s}$$

$$+ \left( \alpha_m^l \delta_{mi} + b_{im}^l \right) \left[ \frac{\partial}{\partial \xi} (\alpha_s^k \delta_{sj} + b_{js}^k) \right] \frac{\partial}{\partial \zeta} D^{lk}(m)_{s}$$

$$+ \left( \alpha_m^l \delta_{mi} + b_{im}^l \right) \left[ \frac{\partial}{\partial \zeta} (\alpha_s^k \delta_{sj} + b_{js}^k) \right] \frac{\partial}{\partial \xi} D^{lk}(m)_{s}$$

In particular the second derivative with respect to two orbital exponents becomes

$$\frac{\partial^2}{\partial \alpha_{p}^{l}, \partial \alpha_{p}^{k}} W_{ij} =$$

$$\sum_{m=1}^{N} \sum_{s=1}^{N} \left[ \delta_{lk} \delta_{mp} \delta_{mi} \delta_{sp} \delta_{sj} D^{lk}(m)_{s} \right] + 2 \delta_{lk} \delta_{mp} \delta_{mi} (\alpha_s^k \delta_{sj} + b_{js}^k) D^{lk}(m)_{s}$$

$$+ \delta_{mp} \delta_{mi} \delta_{sp} \delta_{sj} D^{lk}(m)_{s} + \delta_{sp} \delta_{sj} (1 + \delta_{lk})(\alpha_m^l \delta_{mi} + b_{im}^l) D^{lk}(m)_{s}$$

$$+ \delta_{mp} \delta_{mi} (1 + \delta_{lk})(\alpha_s^k \delta_{sj} + b_{js}^k) D^{lk}(m)_{s} + 2 \delta_{lk} \delta_{sp} \delta_{sj} (\alpha_m^l \delta_{mi} + b_{im}^l) D^{lk}(m)_{s}$$
\[
+ (1 + \delta_{lk})^2(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})(\alpha_{s}^{k} \delta_{sj} + b_{js}^{k})D^{lk}(m,p,p')
\]

and
\[
\frac{\partial^2}{\partial \alpha_p^l \partial \alpha_p^l} W_{ij} = \sum_{m=1}^{N} \sum_{s=1}^{N} \left[ \delta_{mp} \delta_{mi}(\alpha_{s}^{k} \delta_{sj} + b_{js}^{k})D^{lk}(m,p,p')
\right.
\]
\[
+ \delta_{mp'} \delta_{mi} \alpha_{s}^{k} \delta_{sj} + b_{js}^{k})D^{lk}(m,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \alpha_{s}^{k} \delta_{sj} + b_{js}^{k})D^{lk}(m,p,p')
\]

The mixed derivative with respect to orbital and correlation exponents can be found as
\[
\frac{\partial^2}{\partial \alpha_p^l \partial \beta_{pq}^l} W_{ij} = \sum_{m=1}^{N} \sum_{s=1}^{N} \left[ \delta_{lk} \Delta(i, m, p, q)\delta_{sp} \delta_{sj}D^{lk}(m,s)
\right.
\]
\[
+ \delta_{mp} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
\[
+ \delta_{mp'} \delta_{mi} \Delta(j, s; p, q)D^{lk}(m,s) + (1 + \delta_{lk})\Delta(j, s; p, q)(\alpha_{m}^{l} \delta_{mi} + b_{im}^{l})D^{lk}(m,p,p')
\]
The last derivative of $W_{ij}$ with respect to two correlation exponents reads

$$
\frac{\partial^2}{\partial \beta_{p'q'}^k \partial \beta_{pq}^k} W_{ij} =
$$

$$
\sum_{m=1}^{N} \sum_{s=1}^{N} \left[ \delta_{lk} \Delta(i, m; s, q') \Delta(j, s; p', q') D_{lk}^{ij} \right.
$$

$$
+ 2 \delta_{lk} \Delta(i, m; p, q)(\alpha_s^k \delta_{sj} + b_{js}^k) \times
$$

$$
\left[ D_{lk}^{ij} \left( m, p', s, p' \right) + D_{lk}^{ij} \left( m, q', s, q' \right) - D_{lk}^{ij} \left( m, p', s, q' \right) - D_{lk}^{ij} \left( m, q', s, p' \right) \right]
$$

$$
+ \Delta(i, m; p', q') \Delta(j, s; p, q) D_{lk}^{ij} \frac{m}{s}
$$

$$
+ (1 + \delta_{lk}) \Delta(i, m; p, q')(\alpha_m^l \delta_{mi} + b_{im}^l) \times
$$

$$
\left[ D_{lk}^{ij} \left( m, p', s, p' \right) + D_{lk}^{ij} \left( m, q', s, q' \right) - D_{lk}^{ij} \left( m, p', s, q' \right) - D_{lk}^{ij} \left( m, q', s, p' \right) \right]
$$

$$
+ (1 + \delta_{lk}) \Delta(i, m; p', q')(\alpha_m^l \delta_{mi} + b_{im}^l) \times
$$

$$
\left[ D_{lk}^{ij} \left( m, p', s, p' \right) + D_{lk}^{ij} \left( m, q', s, q' \right) - D_{lk}^{ij} \left( m, p', s, q' \right) - D_{lk}^{ij} \left( m, q', s, p' \right) \right]
$$

$$
+ (1 + \delta_{lk})^2 (\alpha_m^l \delta_{mi} + b_{im}^l)(\alpha_s^k \delta_{sj} + b_{js}^k) \times
$$

$$
\left[ D_{lk}^{ij} \left( m, p, p', s, p', p' \right) + D_{lk}^{ij} \left( m, p, q', s, p', p' \right) - D_{lk}^{ij} \left( m, p, p', s, p', q' \right) - D_{lk}^{ij} \left( m, p, q', s, p', p' \right) \right]
$$

$$
+ D_{lk}^{ij} \left( m, q, p', s, q', p' \right) + D_{lk}^{ij} \left( m, q, q', s, q', p' \right) - D_{lk}^{ij} \left( m, q, p', s, q', q' \right) - D_{lk}^{ij} \left( m, q, q', s, q', q' \right)
$$

$$
- D_{lk}^{ij} \left( m, p, p', s, q', q' \right) - D_{lk}^{ij} \left( m, p, q', s, q', q' \right) + D_{lk}^{ij} \left( m, p, p', s, q', q' \right) + D_{lk}^{ij} \left( m, p, q', s, q', q' \right)
$$

$$
- D_{lk}^{ij} \left( m, q, p', s, p', q' \right) - D_{lk}^{ij} \left( m, q, q', s, p', q' \right) + D_{lk}^{ij} \left( m, q, p', s, p', q' \right) + D_{lk}^{ij} \left( m, q, q', s, p', q' \right) \right],
$$

(5.54)
and

\[
\frac{\partial^2}{\partial \beta^l_{p'q'} \partial \beta^l_{pq}} W_{ij} = \\
+ \Delta(i, m; p, q) \left( \alpha^l_p \delta_{s j} + b^l_{i j} \right) \left[ D^{l k} \left( m, p' \right) + D^{l k} \left( m, q' \right) - D^{l k} \left( m, p \right) - D^{l k} \left( m, q \right) \right] \\
+ \Delta(i, m; p', q') \left( \alpha^l_p \delta_{s j} + b^l_{i j} \right) \left[ D^{l k} \left( m, p \right) + D^{l k} \left( m, q \right) - D^{l k} \left( m, p' \right) - D^{l k} \left( m, q' \right) \right] \\
+ (\alpha^l_m \delta_{m i} + b^l_{i m}) \left( \alpha^l_p \delta_{s j} + b^l_{i j} \right) \times \\
\left[ D^{l k} \left( m, p', p' \right) + D^{l k} \left( m, p', q' \right) - D^{l k} \left( m, p, p' \right) - D^{l k} \left( m, p, q' \right) \right] \\
+ D^{l k} \left( m, q', p' \right) + D^{l k} \left( m, q', q' \right) - D^{l k} \left( m, q, p' \right) - D^{l k} \left( m, q, q' \right) \\
- D^{l k} \left( m, p', p' \right) - D^{l k} \left( m, p', q' \right) + D^{l k} \left( m, p, p' \right) + D^{l k} \left( m, p, q' \right) \\
- D^{l k} \left( m, q', p' \right) - D^{l k} \left( m, q', q' \right) + D^{l k} \left( m, q, p' \right) + D^{l k} \left( m, q, q' \right) \right], \tag{5.55}
\]

The last derivative which needs to be considered is the second derivative of the two-body Coulomb integral. The one center two-body Coulomb integral has the form

\[
\langle \omega_l (r_1, r_2, \ldots, r_N) \mid \frac{1}{|r_i - r_j|} | \omega_k (r_1, r_2, \ldots, r_N) \rangle = G_1 G_2 G_3 \tag{5.56}
\]

where

\[
G_1 = \pi^{3(N-2)} \text{det} \left( A^{l k} + B^{l k}; i, j \right)^{-\frac{N}{2}}, \tag{5.57}
\]

\[
G_2 = 2\pi^\frac{N}{2} D'(i, j)^{-1}, \tag{5.58}
\]

and

\[
G_3 = \left[ D'(i) + D'(j) + 2b^{(N-2)}_{ij} \right]^{-\frac{1}{2}} . \tag{5.59}
\]

This form of the Coulombic integral is convenient for our consideration since for the two particle case \(G_1 = 1\), and when all correlation parameters are set to zero \(G_1\) becomes a product of overlap integrals while \(G_2 G_3\) is equal to the Coulombic integral for Gaussian orbitals. The determinant \(\text{det} \left( A^{l k} + B^{l k}; i, j \right)\) does not contain
columns and rows with indexes $i$ and $j$ respectively. To make the notation consistent with our previous nomenclature the above determinant is rewritten as

$$\det(A^l + B^l; i,j) = \det(A^l + B^l|1_{ii},1_{jj}) \equiv D^{lk}(i,j).$$  

(5.60)

The Coulomb integral was obtained as a result of integration (which we called ‘reduction’) over all coordinates except $i$ and $j$. The procedure for reduction is independent of the order of integration and the quantity $b^{(N-2)}_{nm}$ is defined through the following recurrence relation. Let $p_1, p_2, \ldots, p_{N-2}$ be the set of reduction indexes, without $i$ and $j$. Then

$$b^{(1)}_{nm} = b^{(0)}_{nm} - \frac{1}{a_{p_1} + b_{p_1p_1}} b^{(0)}_{np_1} b^{(0)}_{mp_1},$$  

(5.61)

is the result of the first reduction ($b^{(0)}_{nm} \equiv b_{nm}$). After $N-2$ reductions we have

$$b^{(N-2)}_{nm} = b^{(N-3)}_{nm} - \frac{D^{lk}(i,j,p_{N-2})}{D^{lk}(i,j)} b^{(N-3)}_{np_{N-2}} b^{(N-3)}_{mp_{N-2}}.$$  

(5.62)

The quantities $D'(i)$, $D'(j)$ and $D'(i,j)$ are the one- and two-dimensional determinants defined as following

$$D'(i) = a'^{lk}_i + b^{(N-2)}_{ii}, \quad D'(j) = a'^{lk}_j + b^{(N-2)}_{jj},$$

and

$$D'(i,j) = \begin{vmatrix} a'^{lk}_i + b^{(N-2)}_{ii} & b^{(N-2)}_{ij} \\ b^{(N-2)}_{ji} & a'^{lk}_j + b^{(N-2)}_{jj} \end{vmatrix}.$$  

(5.63)

First, let us consider the second derivative of the Coulombic integrals as

$$\frac{\partial^2}{\partial \zeta \partial \xi} \langle \omega_l | \frac{1}{| \mathbf{r}_i - \mathbf{r}_j |} | \omega_k \rangle =$$

$$\left( \frac{\partial^2 G_1}{\partial \zeta \partial \xi} \right) G_2 G_3 + \left( \frac{\partial G_1}{\partial \zeta} \right) \frac{\partial (G_2 G_3)}{\partial \xi} +$$

$$\left( \frac{\partial G_1}{\partial \xi} \right) \frac{\partial (G_2 G_3)}{\partial \xi} + G_1 \frac{\partial^2}{\partial \zeta \partial \xi} (G_2 G_3).$$  

(5.64)

Since,

$$\frac{\partial G_1}{\partial \xi} = - \frac{3}{2} \pi^{-(N-2)} G_1^5 \frac{\partial}{\partial \xi} D^{lk}(i,j),$$

(5.65)
the second derivative of \( G_1 \) with respect to \( \xi \) and \( \zeta \) is

\[
\frac{\partial^2 G_1}{\partial \zeta \partial \xi} = \frac{15}{4} \pi^{-2(N-2)} G_1^2 \left[ \frac{\partial}{\partial \zeta} D^{l_k}(i,j) \right] \left[ \frac{\partial}{\partial \xi} D^{l_k}(i,j) \right] - \frac{3}{2} \pi^{-(N-2)} G_1^\frac{3}{2} \frac{\partial^2}{\partial \zeta \partial \xi} D^{l_k}(i,j),
\]

and

\[
\frac{\partial^2 G_1}{\partial \zeta \partial \xi} = \frac{5}{3} G_1^{-1} \left( \frac{\partial G_1}{\partial \zeta} \right) \left( \frac{\partial G_1}{\partial \xi} \right) - \frac{3}{2} \pi^{-(N-2)} G_1^\frac{3}{2} \frac{\partial^2}{\partial \zeta \partial \xi} D^{l_k}(i,j),
\]

(5.66)

(5.67)

the expression for the second derivative of the Coulombic integral can be simplified to the form

\[
\frac{\partial^2}{\partial \zeta \partial \xi} (\omega_l|1/r_{ij}|\omega_k) = \frac{5}{3} G_1^2 \left( \frac{\partial G_1}{\partial \zeta} \right) \left( \frac{\partial G_1}{\partial \xi} \right) (\omega_l|1/r_{ij}|\omega_k)
+ \frac{1}{G_1} \left( \frac{\partial G_1}{\partial \zeta} \right) \left( \frac{\partial}{\partial \xi} (\omega_l|1/r_{ij}|\omega_k) \right) + \frac{1}{G_1} \left( \frac{\partial G_1}{\partial \zeta} \right) \left( \frac{\partial}{\partial \xi} (\omega_l|1/r_{ij}|\omega_k) \right)
- \frac{3}{2} \pi^{-(N-2)} G_1^\frac{3}{2} (\omega_l|1/r_{ij}|\omega_k) \frac{\partial^2}{\partial \zeta \partial \xi} D^{l_k}(i,j) + G_1 \left( \frac{\partial^2}{\partial \zeta \partial \xi} \right) G_2 G_3.
\]

(5.68)

The first and second derivatives of \( G_2 \) and \( G_3 \) can be evaluated in a straightforward way

\[
\frac{\partial}{\partial \zeta} G_2 = -\frac{1}{2} \pi^{-\frac{3}{2}} G_2^2 \frac{\partial}{\partial \zeta} D'(i,j),
\]

(5.69)

\[
\frac{\partial^2}{\partial \zeta \partial \xi} G_2 = \frac{1}{2} \pi^{-5} G_2^2 \left[ \frac{\partial}{\partial \zeta} D'(i,j) \right] \left[ \frac{\partial}{\partial \xi} D'(i,j) \right] - \frac{1}{2} \pi^{-\frac{5}{2}} G_2^2 \frac{\partial^2}{\partial \zeta \partial \xi} D'(i,j)
\]

(5.70)

while

\[
\frac{\partial}{\partial \zeta} G_3 = -\frac{1}{2} G_3^2 \frac{\partial}{\partial \zeta} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}]
\]

(5.72)

and

\[
\frac{\partial^2}{\partial \zeta \partial \xi} G_3 =
- \frac{1}{4} G_3^{-3} \left( \frac{\partial}{\partial \zeta} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}] \right) \left( \frac{\partial}{\partial \xi} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}] \right)
\]
\[ \frac{\partial^2}{\partial \zeta \partial \xi} G_3 = \]
\[ 3G_3^{-1} \left( \frac{\partial}{\partial \zeta} G_3 \right) \left( \frac{\partial}{\partial \xi} G_3 \right) - \frac{1}{2} G_3^3 \frac{\partial^2}{\partial \zeta \partial \xi} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}]. \]

Finally, the remaining part of the second derivative of the Coulombic integral can be calculated as
\[ G_1 \frac{\partial^2}{\partial \zeta \partial \xi} (G_2 G_3) = \]
\[ -\frac{1}{2} \pi^{-\frac{3}{2}} \langle \omega | 1/r_{ij} | \omega \rangle G_2^2 \left( \pi^{-\frac{3}{2}} \left[ \frac{\partial}{\partial \zeta} D'(i,j) \right] \left[ \frac{\partial}{\partial \xi} D'(i,j) \right] + \frac{\partial^2}{\partial \zeta \partial \xi} D'(i,j) \right) \]
\[ - \frac{1}{4} \pi^{-\frac{3}{2}} \langle \omega | 1/r_{ij} | \omega \rangle \left( \frac{G_2}{G_3} \right)^2 \left( \frac{\partial}{\partial \zeta} D'(i,j) \right) \left( \frac{\partial}{\partial \xi} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}] \right) \]
\[ - \frac{1}{4} \pi^{-\frac{3}{2}} \langle \omega | 1/r_{ij} | \omega \rangle \left( \frac{G_2}{G_3} \right)^2 \left( \frac{\partial}{\partial \zeta} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}] \right) \left( \frac{\partial}{\partial \xi} D'(i,j) \right) \]
\[ - \frac{1}{4} \langle \omega | 1/r_{ij} | \omega \rangle G_3^{-4} \left( \frac{\partial}{\partial \zeta} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}] \right) \times \]
\[ \left( \frac{\partial}{\partial \xi} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}] \right) \]
\[ - \frac{1}{2} \langle \omega | 1/r_{ij} | \omega \rangle G_3^{-2} \frac{\partial^2}{\partial \zeta \partial \xi} [D'(i) + D'(j) + 2b_{ij}^{(N-2)}]. \]

According to our previous section
a) if \( \xi, \) or \( \zeta = \alpha_k^i; \)
\[ \frac{\partial}{\partial \alpha_k^i} D^{lk}(i,j) = D^{lk}(i,j) \]
\[ \frac{\partial}{\partial \alpha_k^i} D^{lk}(i,j) = D^{lk}(i,j) \]
\[ \frac{\partial}{\partial \beta^k_{pq}} D^{lk}(i,j) \]
\[ = D^{lk}(i,j) + D^{lk}(i,j) - D^{lk}(i,j) - D^{lk}(i,j). \]

The derivatives of \( D'(i), D'(j) \) and \( D'(i, j) \) i.e.
\[ \frac{\partial}{\partial \alpha_k^i} D'(i) = (1 + \delta_{lk}) \delta_{pi} + \frac{\partial b_{ii}^{(N-2)}}{\partial \alpha_k^i}; \]
\[ \frac{\partial}{\partial \beta^k_{pq}} D'(i) = \frac{\partial b_{ii}^{(N-2)}}{\partial \beta^k_{pq}}, \]
\[
\frac{\partial}{\partial \alpha_p^k} D'(j) = (1 + \delta_{lk}) \delta_{pj} + \frac{\partial b^{(N-2)}_{ij}}{\partial \alpha_p^k} : \frac{\partial}{\partial \beta_{pq}^k} D'(j) = \frac{\partial b^{(N-2)}_{ij}}{\partial \beta_{pq}^k},
\]
\[
\frac{\partial}{\partial \alpha_p^k} D'(i, j) = \left( \frac{\partial D'(i)}{\partial \alpha_p^k} \right) D'(j) + D'(i) \left( \frac{\partial D'(j)}{\partial \alpha_p^k} \right) - 2b^{(N-2)}_{ij} \frac{\partial b^{(N-2)}_{ij}}{\partial \alpha_p^k},
\]
\[
\frac{\partial}{\partial \beta_{pq}^k} D'(i, j) = \left( \frac{\partial D'(i)}{\partial \beta_{pq}^k} \right) D'(j) + D'(i) \left( \frac{\partial D'(j)}{\partial \beta_{pq}^k} \right) - 2b^{(N-2)}_{ij} \frac{\partial b^{(N-2)}_{ij}}{\partial \beta_{pq}^k},
\]

(5.78)

can be found as first derivative of \( b^{(N-2)}_{nm} \) with respect to \( \xi \)
\[
\frac{\partial}{\partial \xi} b^{(N-2)}_{nm} = \frac{\partial}{\partial \xi} b^{(N-3)}_{nm} - \left( \frac{\partial}{\partial \xi} X \right) b^{(N-3)}_{np} b^{(N-3)}_{mp} \]
\[
- X \frac{\partial^2}{\partial \xi^2} \left( b^{(N-3)}_{np} b^{(N-3)}_{mp} \right),
\]

(5.79)

where
\[
X = D^{lk}(i, j)^{-1} D^{lk}(i, j, p),
\]

(5.80)

and second derivatives with respect to \( \zeta \)
\[
\frac{\partial^2}{\partial \xi \partial \zeta} b^{(N-2)}_{nm} = \frac{\partial^2}{\partial \xi \partial \zeta} b^{(N-3)}_{nm} - \left( \frac{\partial}{\partial \xi} X \right) b^{(N-3)}_{np} b^{(N-3)}_{mp}
\]
\[
- \left( \frac{\partial}{\partial \xi} X \right) b^{(N-3)}_{np} b^{(N-3)}_{mp} - \left( \frac{\partial}{\partial \xi} X \right) \frac{\partial}{\partial \xi} \left( b^{(N-3)}_{np} b^{(N-3)}_{mp} \right)
\]
\[
- X \frac{\partial^2}{\partial \xi \partial \zeta} \left( b^{(N-3)}_{np} b^{(N-3)}_{mp} \right),
\]

(5.81)

The appropriate derivatives of the determinant were discussed in the previous section.

5.4 COMPUTATIONAL IMPLEMENTATION AND NUMERICAL EXAMPLES

The presented second derivatives of the functional \( J[\{\alpha_p^i\}, \{\beta_{pq}^i\}; k] \) with respect to orbital and correlation exponents have been computationally implemented. The implementation of the formulas for the second derivatives of the integrals was
accomplished with the use of the algorithms expressed in terms of the first derivatives and appropriate derivatives of the \((A^{l_k} + B^{l_k})\) determinant discussed in a previous section. This approach made the implementation efficient and transparent. The correctness of the code for the second derivatives was checked for each integral using the finite difference method

\[
\frac{\partial I'(x)}{\partial x} \approx \frac{I'(x + \Delta x) - I'(x)}{\Delta x},
\]

(5.82)

where \(I'(x)\) denotes the appropriate first derivative. The second derivatives of the matrix elements were also verified using the finite difference method. Finally, we verified numerically the value of second derivatives of the variational functional. This was accomplished with the use of fixed values of coefficient \(C_k\) since, as mentioned before, in the present implementation we do not consider the contributions of \(\frac{\partial C_k}{\partial \xi}\) to the second derivative of the functional.

As a numerical example we performed variational nonadiabatic calculations on the \(HD^+\) molecule. For this system we used the following variational wave function

\[
\Psi = \sum_{k=1}^{M} c_k \omega_k(r_D, r_H, r_e) \Theta(D) \Theta(H) \Theta(e),
\]

(5.83)

with the spatial part

\[
\omega_k = \exp \left[-(r_D, r_H, r_e)(A^k + B^k)(r_D, r_H, r_e)^T\right],
\]

(5.84)

In the Eq.(5.83) \(\Theta(D), \Theta(H)\) and \(\Theta(e)\) are spin functions for the deutron, proton and electron respectively. Additionally we assumed that there is no spin coupling between particles. The \(HD^+\) wave function does not possess any permutational symmetry with respect to exchange of particles. In our study we performed calculations with 5, 10, 18 and 36 Gaussian basis functions. The values of internal energy are summarized in the Table IX. Upon examining the data one can see a quite good convergence of the results to the best literature value of \(-0.597897967\ a.u.\) [26]. It would require considerably more Gaussian functions to match this result and such calculations will be performed in the future after the computer code is significantly optimized and transposed to a parallel computer.
All optimization was performed with the use of the IMSL routine DUMIAH which requires the first and second derivatives of the optimized function. The use of the second derivatives dramatically improved the rate of convergence as well as the overall time required to reach the minimum in comparison to the numerical optimization methods used by us before. In Fig. 2 we demonstrated the convergence of the energy in the optimization of all parameters of 18 Gaussian basis functions (108 exponents). The optimization had to be restarted three times due to the fact that the IMSL routine, after making several successful steps was unable to lower the energy any further. However, when restarted from the last point of the previous run the routine was able to make again significant gains.
Fig. 2. The change of the internal energy $E_{\text{Int}}$ during optimization procedure.
TABLE IX. Ground state internal energies (in a. u.) computed with basis set of M functions for the HD⁺ molecule.

<table>
<thead>
<tr>
<th>M</th>
<th>E_{min}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>-0.543 635 455</td>
</tr>
<tr>
<td>10</td>
<td>-0.562 110 188</td>
</tr>
<tr>
<td>18</td>
<td>-0.586 854 300</td>
</tr>
<tr>
<td>36</td>
<td>-0.590 037 755</td>
</tr>
</tbody>
</table>

The best literature value = -0.597 897 967 [43].

5.5 CONCLUSIONS

The development of second derivatives of integrals with explicitly correlated Gaussian type functions with respect to Gaussian exponents constitutes an important step in developing an effective nonadiabatic methodology to treat multiparticle systems. In our initial studies we used numerical optimization of orbital and correlation exponents and the limitations of such an approach were already transparent in calculations on the three body systems. In order to perform accurate variational calculations with longer expansions on systems with more particles the determination of the first and second derivatives of the variational functional with respect to Gaussian exponents is mandatory and the present work has been concerned with the development and implementation of the theory pertaining to this subject. Our preliminary calculations have shown the effectiveness of the Newton-Raphson optimization based on analytical determination of the first and second derivatives.
CHAPTER VI

HIGHER ROTATIONAL STATES

6.1 METHODOLOGY

In the previous Chapters we considered the nonadiabatic ground state of the $N$-particle system with $J = 0$. In this Chapter we would like to present methodology for generating higher nonadiabatic rotational states. Before we demonstrate the procedure for generating higher rotational states let us summarize some results concerning the angular momentum theory.

The total angular momentum operator for the $N$-particle system is defined as (setting $\hbar = 1$)

$$\hat{\mathbf{J}} = -i \sum_{j=1}^{N} \mathbf{r}_j \times \nabla_j,$$

where $\nabla_j$ is the gradient operator associated with the Laboratory Frame (LF) coordinates. The symbol $J$ is used in the BO theory to denote the rigid body rotation angular momentum, and in nonadiabatic theory denotes the total angular momentum. The eigenvalue for the $z$-component of the total angular momentum will be denoted by $M_z$. The $\hat{\mathbf{J}}$ associated with LF coordinates is invariant to any nonsingular linear coordinate transformation defined by

$$\mathbf{r}' = \sum_{j=1}^{N} D_{ij} \mathbf{r}.$$

If the transformation matrix is nonsingular, i.e., $|D| \neq 0$, the inverse transformation can be defined as

$$\mathbf{r} = \sum_{j=1}^{N} D_{ij}^{-1} \mathbf{r}'.$$
With the use of the above relations, the transformation of the gradient can be easily accomplished,

\[ \nabla_i = \sum_{j=1}^{N} \left( \frac{\partial r_j^i}{\partial r_i} \right) \nabla_j' = \sum_{j=1}^{N} D_{ij} \nabla_j', \]  

and the total angular momentum can be transformed as

\[ \hat{\mathbf{J}} = -i \sum_{i=1}^{N} \sum_{j,k=1}^{N} D_{ij}^{-1} D_{kj} r'_j \times \nabla_j' = -i \sum_{j=1}^{N} r'_j \times \nabla_j', \]  

that shows invariance of \( \hat{\mathbf{J}} \) if \( D^{-1} \) exists. Next, let us assume that the transformation from the Cartesian coordinates to the CM coordinates \((\mathbf{R}_{CM}, \rho_1, ..., \rho_{N-1})\) is a nonsingular transformation. Because of the invariance of \( \hat{\mathbf{J}} \), an obvious separation in CM coordinates occurs,

\[ \hat{\mathbf{J}} = \hat{\mathbf{J}}_{c.m.} + \hat{\mathbf{J}}', \]  

where

\[ \hat{\mathbf{J}}_{c.m.} = -i \mathbf{R}_{c.m.} \times \nabla_{\mathbf{R}_{c.m.}}, \]  

and

\[ \hat{\mathbf{J}}' = -i \sum_{j=1}^{N-1} r'_j \times \nabla'_j. \]  

Because the internal Hamiltonian is invariant to infinitesimal rotations about any axis in the noninternal frame of reference, the internal momentum is a conserved quantity.

Having discussed basic properties of the angular momenta, let us now consider the nonadiabatic many-body wave function of the form

\[ \Psi_{TOT} = \sum_{k=1}^{M} C_k P(1, 2, ..., N) |\phi_k(r_1, r_2, ..., r_N)\Theta^N_{S,M}|. \]  

In order to generate a Gaussian cluster function with higher angular momenta, the s-type clusters are multiplied by an appropriate power of the coordinates of the particle positions with respect to the orbital centers, (we already discussed this procedure in the section devoted to the nonadiabatic many body wave function). The conventional way of generating a wave function corresponding to a particular angular
momentum is by restriction of the basis set to functions which are eigenfunctions of
the angular momentum operators, i.e., eigenfunctions of the square of the angular
momentum and its z-component. This cannot be easily accomplished in our case.
Therefore we propose an alternate approach which involves penalty terms introduced
into the variational functional to force the system into the desired internal rotational
state. In order to accomplish this let us consider the following quantities:

\[ W_1 = \sum_{\mu=1}^{M} |\langle \phi_{\mu} | \hat{J}'^2 - J(J+1) | \Psi_{\text{TOT}} \rangle|, \]  
(6.11)

and

\[ W_2 = \sum_{\mu=1}^{M} |\langle \phi_{\mu} | \hat{J}'_z - M_z | \Psi_{\text{TOT}} \rangle|, \]  
(6.12)

where \( \phi_{\mu} \) is an element of a basis set consisting of \( M \) functions, \( J \) is the quantum
number of the desired rotational states, and \( \Psi_{\text{TOT}} \) is the variational wave function.
The above quantities are always positive, or equal to zero. Now we introduce the
quantities \( W_1 \) and \( W_2 \) multiplied by constants \( k_1 \) and \( k_2 \) with positive values into
the variational functional given by the Eq.(6.12)

\[ \hat{F}[\Psi_{\text{TOT}}; k_1, k_2] = \frac{\langle \Psi_{\text{TOT}} | H_{\text{TOT}} - T_{\text{CM}} | \Psi_{\text{TOT}} \rangle + k_1 W_1 + k_2 W_2}{\langle \Psi_{\text{TOT}} | \Psi_{\text{TOT}} \rangle}. \]  
(6.13)

In the process of minimizing the functional (6.13) one can effectively force the system
into the rotational state with quantum numbers \( J \) and \( M \) provided that the basis set
is sufficiently flexible to represent the state. Therefore, at the end of the optimization
not only the condition

\[ \hat{F}[\Psi_{\text{TOT}}] \simeq E_{\text{int}}(J, M_z) \]  
(6.14)

will be fulfilled, where \( E_{\text{int}}(J, M) \) corresponds to the internal energy of the state
with rotation quantum numbers \( J \) and \( M_z \), but also we expect that

\[ \hat{J}'^2 \Psi_{\text{TOT}} \simeq J(J+1) \Psi_{\text{TOT}}, \]  
(6.15)
as well as

\[ J'_z \Psi_{\text{TOT}} \simeq M \Psi_{\text{TOT}}. \]  
(6.16)
6.2. NUMERICAL EXAMPLE

To demonstrate realization of the procedure presented in previous section let us consider a two-particle system with the following Hamiltonian

\[
H_{TOT} = -\frac{1}{2m_1} \nabla_1^2 - \frac{1}{2m_2} \nabla_2^2 - \frac{1}{r_{12}}. \tag{6.17}
\]

After separation of the CM motion the solution of the internal eigenvalue problem can be obtained exactly as

\[
E_n = -\frac{\mu}{2n^2}, \quad n = 1, 2, \ldots,
\]

where \( \mu \) denotes the reduced mass, i.e., \( \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \). For the hydrogen atom one can neglect the motion of the proton since its mass is much bigger than the electron, however for system like \( e^+ e^- \) such approximation can not be made. This point was discussed in the Chapter III in relation to the ground state energy.

In this section we would like to demonstrate that the higher rotational energy can be variationaly calculated directly, using the full Hamiltonian, without explicit separation of the CM motion. The general variational wave function that is considered in this calculation has the following form

\[
\Psi_{TOT} = \sum_{\nu=1}^{M} C_{\nu} x_1^{k_1} y_1^{l_1} z_1^{n_1} x_2^{k_2} y_2^{l_2} z_2^{n_2} \exp(-\alpha_1^{\nu} r_1^2 - \alpha_2^{\nu} r_2^2 - \beta_1^{\nu} r_{12}^2). \tag{6.19}
\]

The evaluation of the integrals involving the Hamiltonian and the above function was demonstrated in the Chapter II. The penalty components of variational functional that should force the system to assume rotational state with particular \( J \) and \( J_z \) could be expressed in terms of generalized overlap integrals, as it is demonstrated in the Appendix D.

In our preliminary calculations we considered the first rotational state for the positronium system with \( J = 1, J_z = 0 \). The corresponding energy is equal to \( E_1 = -6.25 \times 10^{-2} \text{a.u.} \), according to Eq.(6.18), The expectation value of \( J^2 \) for this state is equal to 2. The first rotational state can be generated by restricting of the variational wave function, given by Eq.(6.19), to the following form

\[
\Psi_{TOT} = (z_1 - z_2) \exp(-\alpha r_1^2 - \alpha r_2^2 - \beta r_{12}^2), \tag{6.20}
\]
gives the expectation value of $J^2$ equal to 2 and the expectation value of $J_z$ equal to 0, while the following functions

$$\Psi_{TOT} = (z_1 + z_2) \exp(-\alpha_1^2 r_1^2 - \alpha_2^2 r_2^2 - \beta_{12}^2 r_{12}^2), \quad (6.21)$$

gives states with expectation value of $J^2$ equal to 0.

Next we used 18-functions in expansion

$$\Psi_{TOT} = \sum_{\nu=1}^{8} C_\nu z_1 \exp(-\alpha_1^\nu r_1^2 - \alpha_2^\nu r_2^2 - \beta_{12}^\nu r_{12}^2)$$

$$+ \sum_{\nu=1}^{8} C'_\nu z_2 \exp(-\alpha_1'^\nu r_1^2 - \alpha_2'^\nu r_2^2 - \beta_{12}'^\nu r_{12}^2) \quad (6.22)$$

to perform a variational calculations. One notices that no restrictions have been placed on the relation between $C_\nu$ and $C'_\nu$, $\alpha_1^\nu$ and $\alpha_1'^\nu$, $\alpha_2^\nu$ and $\alpha_2'^\nu$, $\beta_{12}^\nu$ and $\beta_{12}'^\nu$.

After the initial diagonalization of the Hamiltonian, we selected the one eigenvector which corresponded to the wave function with the lowest energy and expectation value of $J^2$ near 2. The procedure for calculating the expectation values of $J^2$ and $J_z$ have been computationally implemented. The calculations of $< J^2 >$ and $< J_z >$ for the functions Eq. (6.20) and Eq. (6.21) produced exactly the correct values, thus validating the computational algorithms. After preliminary optimization we obtain the energy equal to $E = -3.458 \times 10^{-2}$ with expectation value of $J^2$ equal to 2.07502. This result is an indication that more work is required in this area.
CHAPTER VII

SUMMARY AND CONCLUSIONS

7.1 WORK ACCOMPLISHED

The goal of this dissertation was to present a new nonadiabatic approach to molecular systems. In this approach we represented the nonadiabatic many-body wave function in terms of an expansion of explicitly correlated Gaussian functions dependent on the Cartesian coordinates of the positions of the particles in the laboratory frame system. By retaining the Cartesian coordinate frame rather than transforming to the CM coordinate frame we gained a considerable simplification of the quantum representation of the state of the system without making any arbitrary selection of the internal coordinate system, or approximations with regard to the separability of the nuclear and electronic motions. The effectiveness of the proposed methodology utilizing the explicitly correlated Gaussian functions is apparent from the relative ease of its computational implementation [75].

Appropriate multiparticle integrals were derived and computationally implemented. This includes the integrals over functions with higher angular momenta generated with the use of raising operators [76]. For optimization of nonlinear parameters (exponents) that appear in the Gaussian functions, we applied the Newton-Raphson optimization technique which requires evaluation of the first and second derivatives of the variational functional with respect to those parameters [85,86]. Finally, we demonstrated how higher nonadiabatic rotational states can be generated [87].

The presented methodology was applied in nonadiabatic calculations of several model systems. This includes a study of the hydrogen atom and the positronium system to allow comparison with exact solutions of the nonrelativistic Schroedinger equation. Also, nonadiabatic calculations were performed for three particle systems, $H_2^+$ and $HD^+$, as well as the four particle hydrogen molecule. The nonadiabatic
calculations on three particle systems demonstrated that the same level of accuracy can be accomplished with our approach as with the standard methods where the CM and internal motions were separated explicitly through the transformation of the coordinate system. The nonadiabatic calculation becomes significantly more difficult because the number of basis functions used in constructing the wave function and the number of variational parameters increases rapidly. We should note however, that our methodology remains computationally feasible for systems with more than four particles whereas the standard methods become computationally intractable.

For optimization of nonlinear parameters, we implemented and tested three different techniques. In our preliminary calculation we used a numerical method, i.e., the conjugated gradient method. Next we developed a technique with analytical first derivatives, and finally we implemented the Newton-Raphson optimization procedure. Our preliminary results showed that the methodology based on the first and second derivatives is the more effective method and can be used to optimize a large number of Gaussian exponents.

7.2 FUTURE DIRECTIONS

The nonadiabatic corrections are usually very small for molecular systems and exceptions are rare. A meaningful nonadiabatic calculation should be very accurate. By undertaking the effort of developing the “technology” of Gaussian cluster functions for nonadiabatic calculations, we believe that we can accomplish the required level of accuracy and successfully extend the nonadiabatic treatment beyond three particle systems. The calculations for four- and five- particle systems can be carried out in exactly the same way as for three particle systems. This, however, requires much more computational effort. One of the most important directions that will facilitate an application of the nonadiabatic approach to systems with more particles seems to be the derivation and implementation of the first- and second- order derivatives of Gaussian cluster functions with respect to the exponential parameters. As stated above, the preliminary results are encouraging. The
algorithms of the Newton-Raphson optimization scheme and the analytical derivatives are very well suited to a parallel computer system and such an implementation will be pursued in the near future.

Several "even tempering" procedures exist for generating Gaussian orbital exponents and there are a few for generating Gaussian correlation exponents for correlated electronic wave functions. An even tempered procedure is also possible in our approach, however the situation here is significantly more complicated due to the fact that the particles represented by the correlated wave function can have different masses and charges. The development of an even tempered procedure will allow us to greatly reduce the expense of the parameter optimization effort and, in consequence, will allow faster treatment of larger systems.
REDUCTION OF MANY ELECTRON INTEGRALS

The object of this appendix is to demonstrate the evaluation of the function $G(r_i, r_j)$ introduced in Chapter II. We will use the mathematical induction technique to derive its form for an arbitrary number of particles. The general form of this function will be also very helpful for the future evaluation of integrals with higher angular momenta by application of raising operators. In the first step we demonstrate integration over $p$ and $q$ coordinates. Then we demonstrate the structure of the function in the $k$-th step of reduction. Using the last result we demonstrate the form in the $k+1$ step of integration and finally its shape for arbitrary $n$.

To perform the reduction over the $p$-th coordinate, let us first rearrange the quadratic form $rB^\mu_\nu r^T$ as follows

\[ rB^\mu_\nu r^T = r(1, \ldots, N; p)B^\mu_\nu r^T(1, \ldots, N; p) + 2r_p \sum_{m=1 \atop m \neq p}^N b^{\mu\nu}_{mp} r_m + b^{\mu\nu}_{pp} r_p^2 \]  

(A.1)

where $r(1, \ldots, N; p)$ denotes a $N$-dimensional row vector without the $r_p$ coordinate,

\[ r(1, \ldots, N; p) = (r_1, r_2, \ldots, r_{p-1}, 0, r_{p+1}, \ldots, r_N). \]  

(A.2)

Using Eq.(A.1) we may explicitly separate the coordinate $r_p$ ($p \neq i$ and $p \neq j$) in the expression of the function $G(r_i, r_j)$
\[ G(r_i, r_j) = \int \cdots \int \exp \left[ - \sum_{n=1}^{N} a_n^{\mu\nu} [r_n - R_n^{\mu\nu}]^2 - r(1, \ldots, N; p) B_{\mu\nu} r^T(1, \ldots, N; p) \right. \\
\]

\[ + a_p^{\mu\nu} \left( \frac{a_p^{\mu\nu}}{D(p)} - 1 \right) (R_p^{\mu\nu})^2 \\
- 2 \frac{a_p^{\mu\nu}}{D(p)} R_p^{\mu\nu} \sum_{m=1}^{N} b_{mp}^{\mu\nu} r_m + \frac{1}{D(p)} \left( \sum_{m=1}^{N} b_{mp}^{\mu\nu} r_m \right)^2 \int \exp \left[ -D(p)[r_p - Q_p]^2 \right] dr浦dr_1 \ldots dr_N / (i, j), \tag{A.3} \]

where

\[ D(p) = a_p^{\mu\nu} + b_{pp}^{\mu\nu}, \tag{A.4} \]

and

\[ Q_p = \frac{1}{D(p)} \left( a_p^{\mu\nu} R_p^{\mu\nu} - \sum_{m=1}^{N} b_{mp}^{\mu\nu} r_m \right). \tag{A.5} \]

Integrating over \( r_p \), one obtains

\[ G(r_i, r_j) = \pi^{\frac{3}{2}} D^{-\frac{3}{2}}(p) \exp \left[ - \frac{a_p^{\mu\nu} b_{pp}^{\mu\nu}}{D(p)} (R_p^{\mu\nu})^2 \right] \times \]

\[ \int \cdots \int \exp \left[ - \sum_{n=1}^{N} a_n^{\mu\nu} [r_n - R_n^{\mu\nu}]^2 - r(1, \ldots, N; p) B_{\mu\nu} r^T(1, \ldots, N; p) \right. \\
\]

\[ - 2 \frac{2}{D(p)} C_{\mu\nu}(R_p^{\mu\nu}) r^T(1, \ldots, N; p) \int dr_1 \ldots dr_N / (i, j, p), \tag{A.6} \]

with the new matrix \( B'_{\mu\nu} \) whose elements are

\[ b'_{nm}^{\mu\nu} = b_{nm}^{\mu\nu} - \frac{1}{D(p)} b_{np}^{\mu\nu} b_{mp}^{\mu\nu}. \tag{A.7} \]
In the formula (A.6) we have also introduced the new N-dimensional row matrix 
\( C^\mu\nu'(R^\mu\nu_p) \) with the elements

\[
c^\mu\nu_m(R^\mu\nu_p) = a^\mu\nu_p b^\mu\nu_{mp} R^\mu\nu_p. \tag{A.8}
\]

The second step of the reduction is very similar to the first one. After some 
algebraic manipulations we may separate the coordinate \( r_q \) into the new bilinear 
form \( r(1,\ldots,N;p)B^\mu\nu r^T(1,\ldots,N;p), \)

\[
r(1,\ldots,N;p)B^\mu\nu r^T(1,\ldots,N;p) = r(1,\ldots,N;p,q)B^\mu\nu r^T(1,\ldots,N;p,q)
+ 2r_q \sum_{m \neq q} b^\mu\nu_{mq} r_m + b^\mu\nu_{qq} r_q^2. \tag{A.9}
\]

In the last equation we have extended the notation introduced in Chapter II, namely
in the \( r(1,\ldots,N;p,q) \) vector both \( r_p \) and \( r_q \) are set to zero. Substituting the above 
result into Eq.(A.6) and collecting all terms with \( r_q \) one obtains

\[
G(r_i, r_j) = \pi^{\frac{d}{2}} D^{-\frac{d}{2}}(p) \exp \left[ - \frac{a^\mu\nu b^\mu\nu}{D(p)} (R^\mu\nu_p)^2 - a^\mu\nu (R^\mu\nu_q)^2 \right] \times

\int \cdots \int \exp \left[ - \sum_{\substack{n=1 \\ n \neq i,j}}^N a^\mu\nu_n |r_n - R^\mu\nu_n|^2 
\right.

\left. - r(1,\ldots,N;p,q)B^\mu\nu r^T(1,\ldots,N;p,q) \right.

+ \frac{1}{a^\mu\nu_q + b^\mu\nu_{qq}} \left( a^\mu\nu_q R^\mu\nu_q - \sum_{m \neq q} b^\mu\nu_{mq} r_m - \frac{a^\mu\nu b^\mu\nu_{pq}}{D(p)} R^\mu\nu_p \right)^2

\left. - \frac{2}{D(p)} C^\mu\nu'(R^\mu\nu_p)r^T(1,\ldots,N;p,q) \right] \times 

\int \exp \left[ -(a^\mu\nu_q + b^\mu\nu_{qq}) |r_q - Q_{pq}|^2 \right] dr_q dr_1 \ldots dr_N/(i,j,p), \tag{A.10}
\]
with the new $Q_{pq}$ center defined as follows

$$Q_{pq} = \frac{1}{a_q^{\mu\nu} + b_q^{\mu\nu}} \left( a_q^{\mu\nu} R_q^{\mu\nu} - \sum_{m=1}^{N} b_{mq}^{\mu\nu} r_m - \frac{c_2(R_p^{\mu\nu})}{D(p)} \right). \tag{A.11}$$

It is important in our calculation to notice the relation between the appropriate parameters before and after the reduction step. Namely, after some algebraic manipulations, we may find the following relations

$$b_{nm}^{\mu\nu} = \frac{1}{D(p)} \tilde{b}_{nm}^{\mu\nu}, \quad \tilde{b}_{nm}^{\mu\nu} = \begin{vmatrix} D(p) & b_{np}^{\mu\nu} \\ b_{mp}^{\mu\nu} & b_{nm}^{\mu\nu} \end{vmatrix}, \tag{A.12}$$

and

$$a_q^{\mu\nu} + b_q^{\mu\nu} = \frac{D(p, q)}{D(p)}; \quad D(p, q) = \begin{vmatrix} a_p^{\mu\nu} + b_p^{\mu\nu} & b_p^{\mu\nu} \\ a_p^{\mu\nu} + b_p^{\mu\nu} & a_q^{\mu\nu} + b_q^{\mu\nu} \end{vmatrix}. \tag{A.13}$$

Performing integration over $r_q$ in Eq.(A.10) we have

$$G(r_i, r_j) = \pi^3 D^{-\frac{3}{2}}(p, q) \times$$

$$\exp\left[ - \frac{a_p^{\mu\nu} b_p^{\mu\nu}}{D(p)} (R_p^{\mu\nu})^2 - a_q^{\mu\nu} (R_q^{\mu\nu})^2 + \frac{D(p)}{D(p, q)} \left( a_q^{\mu\nu} R_q^{\mu\nu} - \frac{a_p^{\mu\nu} b_p^{\mu\nu}}{D(p)} R_p^{\mu\nu} \right)^2 \right]$$

$$\times \int \int \ldots \int \exp\left[ - \sum_{n \neq 1 \ldots \neq j} a_n^{\mu\nu} |r_n - R_n^{\mu\nu}|^2 \right.$$

$$- r(1, \ldots, N; p, q) B^{\mu\nu} r^T(1, \ldots, N; p, q)$$

$$- \frac{2}{D(p, q)} \left( a_q^{\mu\nu} R_q^{\mu\nu} - \frac{a_p^{\mu\nu} b_p^{\mu\nu}}{D(p)} R_p^{\mu\nu} \right) \sum_{m=1 \ldots \neq q}^{N} \tilde{b}_{mq}^{\mu\nu} r_m$$

$$- \frac{2}{D(p)} C^{\mu\nu}(R_p^{\mu\nu}) r^T(1, \ldots, N; p, q) \right], \tag{A.14}$$

where $b_{nm}^{\mu\nu}$ is defined in a similar way as $b_{nm}^{\mu\nu}$,
\[ b_{nm}^{\mu\nu} = b_{nm}^{\mu\nu} - \frac{D(p)}{D(p,q)} b_{m}^{\mu\nu} b_{n}^{\mu\nu}. \]  

(A.15)

The final result of the two step integration over \( r_p \) and \( r_q \) should be independent on the order of the reduction, i.e., the integration over \( r_p \) then \( r_q \) yields the same result as integration over \( r_q \) then \( r_p \). In the other words, the final expression should be symmetric for subscripts \( p \) and \( q \). In order to demonstrate this let us examine the final form of \( G(r_i, r_j) \):

\[
G(r_i, r_j) = \pi^3 D^{-\frac{3}{2}}(p,q) \exp \left[ \frac{-1}{D(p,q)} (R_p^{\mu\nu}, R_q^{\mu\nu}) S^{\mu\nu}(p,q) (R_p^{\mu\nu}, R_q^{\mu\nu})^T \right] \times 
\int \int \ldots \int \exp \left[ - \sum_{\substack{n=1 \ldots N, \atop n \neq i, j}} a_n^{\mu\nu} |r_n - R_n^{\mu\nu}|^2 \right. \
- r(1, \ldots, N; p, q) B^{\mu\nu} r^T(1, \ldots, N; p, q) \
- \frac{2}{D(p,q)} C^{\mu\nu}(R_p^{\mu\nu}, R_q^{\mu\nu}) r^T(1, \ldots, N; p, q) \right] dr_1 \ldots dr_N / (i, j, p, q), \tag{A.16}
\]

with

\[
S^{\mu\nu}(p, q) = \begin{pmatrix} a_p^{\mu\nu} D(p, q; p) & a_q^{\mu\nu} b_{p q}^{\mu\nu} \\ a_p^{\mu\nu} b_{q p}^{\mu\nu} & a_q^{\mu\nu} D(p, q; q) \end{pmatrix}, \tag{A.17}
\]

and with the following determinants

\[
D(p, q; p) = \begin{vmatrix} b_{p p}^{\mu\nu} & b_{p x}^{\mu\nu} \\ b_{x p}^{\mu\nu} & a_x^{\mu\nu} + b_{x q}^{\mu\nu} \end{vmatrix}, \quad D(p, q; q) = \begin{vmatrix} a_p^{\mu\nu} + b_{p p}^{\mu\nu} & b_{p q}^{\mu\nu} \\ b_{q p}^{\mu\nu} & b_{q q}^{\mu\nu} \end{vmatrix}. \tag{A.18}
\]

The new row matrix \( C^{\mu\nu}(R_p^{\mu\nu}, R_q^{\mu\nu}) \) obtained as a result of the second step of the reduction has the following elements

\[
c_m^{\mu\nu}(R_p^{\mu\nu}, R_q^{\mu\nu}) = a_p^{\mu\nu} \tilde{c}_m^{\mu\nu} R_p^{\mu\nu} + a_q^{\mu\nu} \tilde{c}_m^{\mu\nu} R_q^{\mu\nu}, \tag{A.19}
\]

and

\[
\tilde{b}_{m p}^{\mu\nu} = \begin{vmatrix} b_{m p}^{\mu\nu} & b_{m q}^{\mu\nu} \\ b_{q p}^{\mu\nu} & a_q^{\mu\nu} + b_{q q}^{\mu\nu} \end{vmatrix}; \quad \tilde{b}_{m q}^{\mu\nu} = \begin{vmatrix} a_p^{\mu\nu} + b_{p p}^{\mu\nu} & b_{p q}^{\mu\nu} \\ b_{q p}^{\mu\nu} & b_{q q}^{\mu\nu} \end{vmatrix}. \tag{A.20}
\]

Finally, the coefficient in the quadratic form, \( b_{nm}^{\mu\nu} \), after same manipulations, becomes
\[ b_{nm}^{\mu \nu} = \frac{1}{D(p, q)} \begin{vmatrix} a_p^{\mu \nu} + b_p^{\mu \nu} & b_{pq}^{\mu \nu} & b_{np}^{\mu \nu} \\ b_{pq}^{\mu \nu} & a_q^{\mu \nu} + b_q^{\mu \nu} & b_{mq}^{\mu \nu} \\ b_{np}^{\mu \nu} & b_{mq}^{\mu \nu} & a_m^{\mu \nu} + b_m^{\mu \nu} \end{vmatrix}. \] (A.21)

Thus it can be seen that indeed the expression for \( G(r_i, r_j) \) is fully symmetric with respect to the \( p \) and \( q \) indices. This property will be helpful in the next part of this section. The procedure exemplifies the general strategy in reduction of many-particle integrals to elementary integrals.

The reduction to the \( k \)-th step proceeds similarly, but of course it becomes more complicated due to the additional terms which arise from the previous steps of the integration. After careful examination of the previous results, we notice that each one-particle reduction gives two types of contributions to the \( G(r_i, r_j) \) function; the first type is the pre-integral term which depends on the orbital and correlation parameters, and an exponential term which is a function of the orbital centers. The second type of the contribution is due to the linear and quadratic terms in the \( r \)-th variable. Let us suppose that reduction on \( N \)-particle integrals has been performed over \( r_1, r_2, \ldots, r_k \) coordinates. Let \( \{l_i\} \) be a set of indexes for these coordinates and \( \text{card}\{l_i\} = k \). Based on the above observations and the general properties of integrals containing Gaussian functions we deduce the form of the function \( G(r_i, r_j) \) after \( k \) steps.

\[ G(r_i, r_j) = \pi^{\frac{3k}{2}} D\left(\{l_i\}\right) \times \exp \left[ -\frac{1}{D(\{l_i\})} (R_{l_1}^{\mu \nu}, \ldots, R_{l_k}^{\mu \nu}) S^{k}(\{l_i\})(R_{l_1}^{\mu \nu}, \ldots, R_{l_k}^{\mu \nu})^T \right] \times \int \int \ldots \int \exp \left[ -\sum_{n=1}^{N} a_n |r_n - R_n^{\mu \nu}|^2 \right. \\
- r(1, \ldots, N; \{l_i\}) B^{(k)} r^T (1, \ldots, N; \{l_i\}) \\
- \frac{2}{D(\{l_i\})} C^{(k)} (R_{l_1}^{\mu \nu}, \ldots, R_{l_k}^{\mu \nu}) r^T (1, \ldots, N; \{l_i\}) \bigg] \text{d}r_1 \ldots \text{d}r_N/(\{l_i\}). \] (A.22)

One may verify that the above equation is true for \( k = 1 \) and \( k = 2 \) by comparing Eqs (A.6) and (A.16). In the last formula we extended the previously introduced notation, namely \( D(\{l_i\}) \) is a \( k \)-th dimensional determinant where each diagonal element is a sum of the orbital coefficient \( a_{l_n} \) and the diagonal correlation coefficient...
while the off-diagonal elements are simply $b_{l_n l_m}$. $(R^{\mu \nu}_{l_1}, \ldots, R^{\mu \nu}_{l_k})$ is a $k$-th dimensional vector with elements $R^{\mu \nu}_{l_1}, \ldots, R^{\mu \nu}_{l_k}$. The square matrix $S^{(k)}(\{l_i\})$ has the following structure: $l_n$-th diagonal elements are equal to $a_{l_n}D(\{l_i\}; l_n)$, where index $l_n$ after semicolon indicates that the determinant $D(\{l_i\})$ is without the $a_{l_n}$ element while off-diagonal elements are $a_{l_n}a_{l_m}b^{(k-2)}_{l_n l_m}$, (see the Eq.(A.17)). The correlation matrix elements are expressed by the following sequence

$$b^{(k)}_{nm} = \frac{1}{D(l_1, \ldots, l_{k-1}, l_k)} \tilde{b}^{(k)}_{nm},$$

$$\tilde{b}^{(k)}_{nm} = D(l_1, \ldots, l_{k-1}, l_k)b^{(k-1)}_{nm} - D(l_1, \ldots, l_{k-1})b^{(k-1)}_{nl_k}b^{(k-1)}_{ml_k}.$$  \hspace{1cm} (A.23)

Moreover, the $\tilde{b}^{(k)}_{nm}$ coefficient may be also rewritten as the following determinant

$$\tilde{b}^{(k)}_{nm} = \begin{vmatrix} b_{l_1 l_1} & b_{l_1 l_2} & \cdots & b_{l_1 n} \\ b_{l_2 l_1} & b_{l_2 l_2} & \cdots & b_{l_2 n} \\ \vdots & \vdots & \ddots & \vdots \\ b_{l_n l_1} & b_{l_n l_2} & \cdots & b_{l_n n} \end{vmatrix}.$$ \hspace{1cm} (A.24)

Finally, the $C^{(k)}$ matrix elements are

$$c^{(k)}_m(R^{\mu \nu}_{l_1}, \ldots, R^{\mu \nu}_{l_k}) = \sum_{l_i = l_1}^{l_k} a_{l_i} \tilde{b}^{(k-1)}_{ml_i} R^{\mu \nu}_{l_i}.$$ \hspace{1cm} (A.25)

Next we will prove that the result is true in the $k+1$ step of the integration based on the $k$-th step. Let us pick up for example the $r_s$ coordinate and then separate all $r_s$-dependent terms from the rest.

$$G(r_i, r_j) = \pi^{\frac{n_b}{2}} D^{\frac{3}{2}}(\{l_i\}) \times$$

$$\exp \left[ \frac{-1}{D(\{l_i\})}(R^{\mu \nu}_{l_1}, \ldots, R^{\mu \nu}_{l_k})S^{(k)}(\{l_i\})(R^{\mu \nu}_{l_1}, \ldots, R^{\mu \nu}_{l_k})^T - a_s(R^{\mu \nu}_s)^2 \right] \times$$
\[
\int \ldots \int \exp \left[ \sum_{n=1}^{N} a_n^{\mu\nu} |r_n - R_n^{\mu\nu}|^2 \right.
\]
\[- r(1, \ldots, N; \{l_i\}, s) B^{(k)} r^T(1, \ldots, N; \{l_i\}, s) \]
\[+ \frac{1}{a_s + b_{ss}^{(k)}} \left( a_s R_s^{\mu\nu} - \sum_{m=1, m \neq (l_i), s}^{N} b_{m}^{(k)} r_m - \frac{1}{D(\{l_i\})} l_k \sum_{i=l_i} a_{l_i} b_{s l_i}^{(k-1)} R_{l_i}^{\mu\nu} \right)^2 \]
\[- \frac{2}{D(\{l_i\})(R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu}) r^T(1, \ldots, N; \{l_i\}, s)} \times \]
\[\int \exp \left[ -(a_s + b_{ss}^{(k)}) r_s - Q_{\{l_i\}, s} \right] dr_s dr_1 \ldots dr_N / (\{l_i\}) \],

(A.26)

The new \( Q_{\{l_i\}, s} \) reads

\[
Q_{\{l_i\}, s} = \frac{1}{a_s + b_{ss}^{(k)}} \left( a_s R_s^{\mu\nu} - \sum_{m=1, m \neq (l_i), s}^{N} b_{m}^{(k)} r_m - \frac{1}{D(\{l_i\})} l_k \sum_{i=l_i} a_{l_i} b_{s l_i}^{(k-1)} R_{l_i}^{\mu\nu} \right). \tag{A.27}
\]

Again, after integration over the \( r_s \) coordinate we obtain the result

\[
G(r_i, r_j) = \pi^2 \frac{(k+1)}{2} \left[ (a_s + b_{ss}^{(k)}) D(\{l_i\}) \right]^{-\frac{3}{2}} \times \]
\[\exp \left[ \left( \frac{1}{D(\{l_i\})(R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu}) S^{(k)}(\{l_i\})(R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu}) r^T - a_s (R_s^{\mu\nu})^2 \right. \]
\[+ \frac{1}{a_s + b_{ss}^{(k)}} \left( a_s R_s^{\mu\nu} - \frac{1}{D(\{l_i\})} l_k \sum_{i=l_i} a_{l_i} b_{s l_i}^{(k-1)} R_{l_i}^{\mu\nu} \right)^2 \right] \times \]
\[\int \ldots \int \exp \left[ \sum_{n=1}^{N} a_n |r_n - R_n^{\mu\nu}|^2 \right.
\]
\[- r(1, \ldots, N; \{l_i\}, s) B^{(k)} r^T(1, \ldots, N; \{l_i\}, s) + \]
\[
\frac{-2}{a_s + b_{ss}^{(k)}} \left( a_s R_{s}^{\mu \nu} - \frac{1}{D(\{l_i\})} \sum_{l_i=l_1}^{l_k} a_{l_i} \delta_{s l_i} R_{l_i}^{\mu \nu} \right) \left( \sum_{m=1, m \neq \{l_i\}, s}^{N} b_{m s}^{(k)} \mathbf{r}_m \right) \\
+ \frac{1}{a_s + b_{ss}^{(k)}} \left( \sum_{m=1, m \neq \{l_i\}, s}^{N} b_{m s}^{(k)} \mathbf{r}_m \right)^2
\]

\[
- \frac{2}{D(\{l_i\})} C^{(k)}(R_{l_1}^{\mu \nu}, \ldots, R_{l_k}^{\mu \nu}) \mathbf{r}^T(1, \ldots, N; \{l_i\}, s) \left[ \frac{1}{D(\{l_i\})} \times \left[ (-1)^{l_1+s} b_{l_1 s} \Delta_1 + (-1)^{l_2+s} b_{l_2 s} \Delta_2 + \ldots + (a_s + b_{ss}) D(\{l_i\}) \right] \right], \tag{A.28}
\]

Consider now the sum of the coefficients \(a_s + b_{ss}^{(k)}\). According to Eq. (3.30) the coefficient \(b_{ss}^{(k)}\) associated with \(b_{ss}^{(k)}\) may be expanded in terms of the elements of the last column (or the last row), namely \(b_{ss}^{(k)} = (-1)^{l_1+s} b_{l_1 s} \Delta_1 + (-1)^{l_2+s} b_{l_2 s} \Delta_2 + \ldots + b_{ss} D(\{l_i\})\). With this expansion the sum of the coefficients \(a_s + b_{ss}^{(k)}\) becomes

\[
a_s + b_{ss}^{(k)} = \frac{1}{D(\{l_i\})} \times \left[ (-1)^{l_1+s} b_{l_1 s} \Delta_1 + (-1)^{l_2+s} b_{l_2 s} \Delta_2 + \ldots + (a_s + b_{ss}) D(\{l_i\}) \right], \tag{A.29}
\]

and it is not difficult to recognize that the expression in the square bracket is an expansion of the determinant \(D(\{l_i\}, s)\)

\[
a_s + b_{ss}^{(k)} = \frac{D(\{l_i\}, s)}{D(\{l_i\})}. \tag{A.30}
\]

Using the above result we may find that the new quadratic form in the \(k+1\) step takes the form

\[
-r(1, \ldots, N; \{l_i\}, s) \mathbf{B}^{(k)} \mathbf{r}^T(1, \ldots, N; \{l_i\}, s) + \frac{D(\{l_i\})}{D(\{l_i\}, s)} \left( \sum_{m=1, m \neq \{l_i\}, s}^{N} b_{m s}^{(k)} \mathbf{r}_m \right)^2
\]

\[
- r(1, \ldots, N; \{l_i\}, s) \mathbf{B}^{(k+1)} \mathbf{r}^T(1, \ldots, N; \{l_i\}, s) \tag{A.31}
\]

with

\[
b_{nm}^{(k+1)} = b_{nm}^{(k)} - \frac{D(\{l_i\})}{D(\{l_i\}, s)} b_{ns}^{(k)} b_{ms}^{(k)}. \tag{A.32}
\]

By substituting equations (A.30) and (A.31) into integral Eq. (A.27), the functions \(G(\mathbf{r}_i, \mathbf{r}_j)\) simplifies to
\[ G(r_i, r_j) = \pi^\frac{3(k+1)}{2} D^{-\frac{3}{2}}(\{l_i\}, s) \times \]

\[
\exp \left[ -\frac{1}{D(\{l_i\})} \left( R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu} \right) S^{(k)}(\{l_i\})(R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu})^T \right] - a_s \left( 1 - \frac{D(\{l_i\})a_s}{D(\{l_i\}, s)} \right) (R_{l_i}^{\mu\nu})^2 - \frac{2a_s}{D(\{l_i\}, s)} R_{l_i}^{\mu\nu} \sum_{l_i=1}^{l_k} a_{l_i} \tilde{b}_{s_{l_i}}^{(k-1)} R_{l_i}^{\mu\nu} \\
+ \frac{1}{D(\{l_i\}, s)D(\{l_i\})} \left( \sum_{l_i=1}^{l_k} a_{l_i} \tilde{b}_{s_{l_i}}^{(k-1)} R_{l_i}^{\mu\nu} \right)^2 \times \]

\[
\int \ldots \int \exp \left[ - \sum_{n=1}^{N} a_n |r_n - R_{l_i}^{\mu\nu}|^2 \
- r(1, \ldots, N; \{l_i\}, s) B^{(k+1)} r^T (1, \ldots, N; \{l_i\}, s) + \\
- \frac{2a_s}{D(\{l_i\}, s)} R_{l_i}^{\mu\nu} \sum_{m=1}^{N} \tilde{b}_{m_{l_i}}^{(k)} r_m - \frac{2}{D(\{l_i\}, s)} \sum_{l_i=1}^{l_k} a_{l_i} R_{l_i}^{\mu\nu} \times \]

\[
\sum_{m=1, m \neq \{l_i\}, s}^{N} \left( \frac{D(\{l_i\}, s) \tilde{b}_{m_{l_i}}^{(k-1)} - \tilde{b}_{l_i,s}^{(k-1)} \tilde{b}_{m,s}^{(k)}}{D(\{l_i\})} \right) r_m \right] dr_1 \ldots dr_N/(\{l_i\}, s). \tag{A.33} \]

Now, we simplify the result further by defining a new set parameters as functions of old parameters. The Appendix B sketches the evaluation of relations between such parameters and

\[
\frac{D(\{l_i\}, s) \tilde{b}_{m_{l_i}}^{(k-1)} - \tilde{b}_{l_i,s}^{(k-1)} \tilde{b}_{m,s}^{(k)}}{D(\{l_i\})} = \tilde{b}_{m_{l_i}}^{(k)}. \tag{A.34} \]

Finally we obtain the following result after reduction over k+1 steps

\[ G(r_i, r_j) = \pi^\frac{3(k+1)}{2} D^{-\frac{3}{2}}(\{l_i\}, s) \times \]

\[
\exp \left[ -\frac{1}{D(\{l_i\}, s)} \left( R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu}, R_{s}^{\mu\nu} \right) S^{(k)}(\{l_i\}, s)(R_{l_1}^{\mu\nu}, \ldots, R_{l_k}^{\mu\nu}, R_{s}^{\mu\nu})^T \right] \times \]
\[
\iiint \ldots \int \exp \left[ - \sum_{n=1}^{N} a_n |r_n - R_n^{\mu \nu}|^2 - r(1, \ldots, N; \{l_i\}, s)B^{(k+1)}T(1, \ldots, N; \{l_i\}, s) - \frac{2}{D(\{l_i\}, s)} \times C^{(k+1)}(R_i^{\mu \nu}, \ldots, R_i^{\mu \nu}, R_s^{\mu \nu})T(1, \ldots, N; \{l_i\}, s) \right] dr_1 \ldots dr_N / (\{l_i\}, s), \quad (A.35)
\]
which concludes our proof.

Using the above result we will perform reduction of many particle integrals into the elementary integrals. After N-2 integrations the \(G(r_i, r_j)\) function becomes

\[
G(r_i, r_j) = \pi^{3(N-2)/2} \left[ \det(\mathbf{A}^{\mu \nu} + \mathbf{B}^{\mu \nu}; i, j) \right]^{-3/2} \times
\]

\[
\exp \left[ - \frac{1}{\det(\mathbf{A}^{\mu \nu} + \mathbf{B}^{\mu \nu}; i, j)} \times \right]
\]

\[
(R_i^{\mu \nu}, \ldots, R_N^{\mu \nu}; i, j)S(1, \ldots, N; i, j)(R_1^{\mu \nu}, \ldots, R_N^{\mu \nu}; i, j)^T \times
\]

\[
\exp \left( -b_{ii}^{(N-2)} r_i^2 - b_{jj}^{(N-2)} r_j^2 - 2b_{ij}^{(N-2)} r_i r_j \right) \times
\]

\[
\exp \left( - \frac{2}{\det(\mathbf{A}^{\mu \nu} + \mathbf{B}^{\mu \nu}; i, j)} \times \right)
\]

\[
\left[ \sum_{n=1}^{N-2} a_n^{\mu \nu} b_{in}^{(N-3)} R_n^{\mu \nu} + r_j \sum_{n'=1}^{N-2} c_{n'}^{\mu \nu} b_{j'n'}^{(N-3)} R_{n'}^{\mu \nu} \right]. \quad (A.36)
\]

The above final formulae is fully symmetric with respect to numbering the particles, as one expects it to be. As we pointed out before, with all nonlinear correlation parameters set to zero, the function \(G(r_i, r_j)\) becomes a simple product of the overlap integrals over Gaussian orbitals.
APPENDIX B

RECCURENCE RELATION BETWEEN $\tilde{j}_{mli}^{(k)}$ COEFFICIENTS

In this appendix we sketch the evaluation of the relation between coefficients which appear in Eq.(A.34), namely we would like to demonstrate that the coefficient $c$ defined as

$$c = \frac{D(\{l_i\}, s) \tilde{j}_{mli}^{(k-1)} - \tilde{j}_{lis}^{(k-1)} \tilde{j}_{mss}^{(k)}}{D(\{l_i\})}, \quad (B.1)$$

is equal to $\tilde{j}_{mli}^{(k)}$. Expanding coefficients in the above formula according to the Eq.(A.24) we found respectively

$$D(\{l_i\}, s) = \begin{pmatrix} (l_1, \ldots, l_k) \\ b_{l_1s} & b_{l_2s} \\ & \vdots \\ b_{l_{1s}} & b_{l_{2s}} & \ldots & a_s + b_{ss} \end{pmatrix} = 0$$

$$\sum_{p=1}^{k} (-1)^{l_p + s} b_{l_p s} \Delta_p + (a_s + b_{ss}) D(\{l_i\}), \quad (B.2)$$

$$\tilde{j}_{mli}^{(k-1)} = \begin{pmatrix} (l_1, \ldots, l_{k-1}) \\ b_{l_{1l}i} & b_{l_{2l}i} \\ & \vdots \\ b_{l_{1m}i} & b_{l_{2m}i} & \ldots & b_{i_{mi}} \end{pmatrix} = 0$$

$$\sum_{j=1}^{k-1} (-1)^{l_j + m} b_{l_{jm}i} \Delta_j + b_{l_{im}i} D(\{l_i - 1\}), \quad (B.3)$$
Substituting the above expansions into Eq.(B.1) one obtains
\[
c = D({l_i})^{-1} \sum_{p=1}^{k} \sum_{j=1}^{k-1} (-1)^{l_p+1} (-1)^{l_j} \Delta_p \Delta_j^* +
\]
\[
D({l_i})^{-1} D({l_i - 1}) \sum_{p=1}^{k} (-1)^{l_p} [(-1)^s b_{i,s} b_{l_j,s} - (-1)^m b_{l_j,m} b_{i,s}] \Delta_p \Delta_j^* +
\]
\[
\sum_{j=1}^{k-1} (-1)^{l_j} [(-1)^m (a_s + b_{s,s}) b_{l_j,m} - (-1)^s b_{m,s} b_{l_j,s}] \Delta_j^* +
\]
\[
[(a_s + b_{s,s}) b_{l_i,m} - b_{m,s} b_{l_i,s}] D({l_i - 1}).
\]

After some tedious algebra the last expansion may be rewritten as follows
\[
c = \begin{vmatrix}
(l_1, \ldots, l_k) & b_{l_1,l_i} & b_{l_1,l_i} \\
\vdots & \vdots & \vdots \\
(b_{l_1,s} & b_{l_2,s} & \ldots & b_{l_1,s})
\end{vmatrix},
\]
\[
(B.7)
\]

and therefore, according to the Eq.(A.24), \( c = \tilde{g}_{ml_i}^{(k)} \).
APPENDIX C

KINETIC ENERGY OF CM MOTION FOR $H_2^+$ MOLECULE

In this appendix we will demonstrate the evaluation of the kinetic energy of the center-of-mass motion for the $H_2^+$ system. Since for spherical Gaussian cluster functions $\langle T_{CM} \rangle = \langle T^x_{CM} \rangle + \langle T^y_{CM} \rangle + \langle T^z_{CM} \rangle = 3\langle T^z_{CM} \rangle$ we only need to consider one type of integral. After integrating $\langle T^z_{CM} \rangle$ over $y_A, y_B, y_1, z_A, z_B$ and $z_1$ coordinates, the expression takes the form

$$\langle T^z_{CM} \rangle = -\frac{\pi}{2M} \sum_{l=1}^M \sum_{k=1}^M c_l c_k D_{lk}(A, B, 1)^{-1} \times \left[ (\omega_l) \frac{\partial^2}{\partial x_A^2} + \frac{\partial^2}{\partial x_B^2} + \frac{\partial^2}{\partial x_1^2} + 2 \left( \frac{\partial \omega_A}{\partial x_A} \frac{\partial}{\partial x_B} + \frac{\partial \omega_A}{\partial x_1} \frac{\partial}{\partial x_B} + \frac{\partial \omega_A}{\partial x_1} \frac{\partial}{\partial x_1} \right) |\omega_k| \right], \quad (C.1)$$

where

$$D_{lk}(A, B, 1) = \begin{bmatrix} a_{1l}^k + b_{1l}^k & b_{1l}^k & b_{1l}^k \\ b_{1l}^k & a_{1l}^k + b_{1l}^k & b_{1l}^k \\ b_{1l}^k & b_{1l}^k & a_{1l}^k + b_{1l}^k \end{bmatrix}. \quad (C.2)$$

All integrals appearing in the Eq. (C.1) can be evaluated using a modification of a previously demonstrated method. Let us take into consideration the general multi-center and multi-particle wave function and the integral

$$I_{ij}^{lk} = \int \ldots \int [\nabla_i \omega_l(r_1, r_2, \ldots r_N)] [\nabla_j \omega_k(r_1, r_2, \ldots r_N)] dr_1 dr_2 \ldots dr_N. \quad (C.3)$$

After performing differentiation with respect to the coordinates of the i-th and j-th particles, followed by some manipulations we get
\[ I_{ij}^{lk} = 4K_{lk} \times \]
\[
\left[ \alpha_i^l \alpha_j^k J(r_i, r_j; 1, 1) - \alpha_i^l \alpha_j^k R_i^k J(r_j, r_i; 1, 0) - \alpha_i^l \alpha_j^k R_j^k J(r_i, r_i; 1, 0) + \right.
\]
\[
\alpha_i^l \alpha_j^k R_i^k R_j^k J(r_i, r_i; 0, 0) + \alpha_i^l \sum_{s=1}^{N} b_{js}^k J(r_i, r_s; 1, 1) +
\]
\[
\alpha_j^k \sum_{m=1}^{N} b_{im}^l J(r_j, r_m; 1, 1) - \alpha_j^k R_i^k \sum_{s=1}^{N} b_{js}^k J(r_i, r_s; 0, 1) -
\]
\[
\alpha_j^k R_j^k \sum_{m=1}^{N} b_{im}^l J(r_i, r_m; 0, 1) + \sum_{m=1}^{N} \sum_{s=1}^{N} b_{im}^l b_{js}^k J(r_m, r_s; 1, 1) \right].
\]

Integrating by parts Eq. (C.1) and introducing integrals Eq. (C.3) one obtains

\[ \langle T_{CM} \rangle = \frac{3\pi}{2M} \sum_{l=1}^{M} \sum_{k=1}^{M} c_l c_k D_{lk}(A, B, 1)^{-1} \times \]
\[
\left[ I_{AA}^{lk} + I_{BB}^{lk} + I_{11}^{lk} + 2(I_{AB}^{lk} + I_{BA}^{lk} + I_{B1}^{lk}) \right].
\]

Because our three-body variational wave function is spherically symmetric, further simplification takes place in the expansion for the particular integral in Eq. (C.5), namely all terms containing the center positions vanish. Additionally, three-dimensional general overlap integrals are replaced by appropriate one-dimensional integrals. For example the integral \( I_{AB}^{lk} \) reads

\[ I_{AB}^{lk} = 4 \left[ \alpha_A^l \alpha_B^k J(x_A, x_B; 1, 1) + \alpha_A^l \sum_{s=A,B} b_{s}^k J(x_A, x_s; 1, 1) + \right. \]
\[
\left. \alpha_B^k \sum_{m=A,B} b_{Am}^l J(x_B, x_m; 1, 1) + \sum_{m=A,B} \sum_{s=A,B} b_{Am}^l b_{Bs}^k J(x_m, x_s; 1, 1) \right].
\]
In this Appendix we will demonstrate the matrix elements for $\hat{J}^2$ and $\hat{J}_z$ operators which are present in the variational functional for generating of higher nonadiabatic rotational states. Since the angular momentum operators contain differentiation with respect to particle coordinates, all required elements can be expressed in terms of the generalized overlap integral. The spherical Gaussian functions as well as the general cluster Cartesian function can be expressed as product of one-dimensional components

$$\omega_\nu = \omega_\nu^{(x)} \omega_\nu^{(y)} \omega_\nu^{(z)},$$  \hspace{1cm} (D.1a)

where

$$\omega_\mu = \exp\left(-\sum_{i=1}^N \alpha_\mu^i |x_i - R_{a,z}^\mu|^2 - \sum_{i=1}^N \sum_{j>i}^N \beta_{ij}^\mu |x_i - x_j|^2 \right).$$  \hspace{1cm} (D.1b)

and

$$\phi_\nu = \phi_\nu^{(x)} \phi_\nu^{(y)} \phi_\nu^{(z)}.$$  \hspace{1cm} (D.2a)

where

$$\phi_\mu = \prod_{s=1}^N \left[(x_s - R_{a,s}^\mu)^{0,0} \right] \omega_\mu,$$  \hspace{1cm} (D.2b)

Using the above properties the matrix element $\langle \phi_\mu | \hat{J}_z^2 | \phi_\nu \rangle$ can be expressed

$$\langle \phi_\mu | \hat{J}_z^2 | \phi_\nu \rangle = -\sum_{i=1}^N \sum_{j=1}^N (\phi_\mu^{(x)} | \phi_\nu^{(x)}) \times$$
\[
\left[ \langle \phi^{(y)}_{\mu} | y_i y_j | \phi^{(y)}_{\nu} \rangle \langle \phi^{(z)}_{\mu} \right| \frac{\partial}{\partial z_i} \frac{\partial}{\partial z_j} | \phi^{(z)}_{\nu} \rangle - \langle \phi^{(y)}_{\mu} | y_i | \phi^{(y)}_{\nu} \rangle \langle \phi^{(z)}_{\mu} \right| \frac{\partial}{\partial z_i} | z_j | \phi^{(z)}_{\nu} \rangle - \\
\langle \phi^{(y)}_{\mu} | \frac{\partial}{\partial y_i} y_j | \phi^{(y)}_{\nu} \rangle \langle \phi^{(z)}_{\mu} | z_i \frac{\partial}{\partial z_j} | \phi^{(z)}_{\nu} \rangle + \langle \phi^{(z)}_{\mu} | z_i z_j | \phi^{(z)}_{\nu} \rangle \langle \phi^{(y)}_{\mu} \right| \frac{\partial}{\partial y_i} \frac{\partial}{\partial y_j} | \phi^{(y)}_{\nu} \rangle].
\]

Using the following relation

\[
z_q (z_q - R_{q,z}^{\nu})^{n_q^{\nu}} = (z_q - R_{q,z}^{\nu})^{n_q^{\nu}+1} + R_{q,z}^{\nu} (z_q - R_{q,z}^{\nu})^{n_q^{\nu}},
\]

the term \(z_q \phi^{(z)}_{\nu}\) can be rearranged as follows

\[
z_q \phi^{(z)}_{\nu} = \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu}+\delta_{s,q}} \right] \omega^{(z)}_{\nu} + R_{q,z}^{\nu} \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu}} \right] \omega^{(z)}_{\nu},
\]

where \(\delta_{s,q}\) denotes the Kronecker delta. One can notice that differentiation of the cluster function with respect to \(z_i\) coordinates is equal to

\[
\frac{\partial}{\partial z_i} \phi^{(z)}_{\nu} = n_{i}^{\nu} \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu} - \delta_{s,i}} \right] \omega^{(z)}_{\nu} - 2 \left[ \alpha_i^{\nu} (z_i - R_{i,z}^{\nu}) + \sum_{n=1}^{N} b_{ui}^{\nu} z_u \right] \phi^{(z)}_{\mu},
\]

and according to the Eq.(D.4) can be rearrange to the form

\[
\frac{\partial}{\partial z_i} \phi^{(z)}_{\nu} = n_{i}^{\nu} \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu} - \delta_{s,i}} \right] \omega^{(z)}_{\nu} - 2 \sum_{n=1}^{N} b_{u_i}^{\nu} \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu} + \delta_{s,u}} \right] \omega^{(z)}_{\nu} - 2 \sum_{n=1}^{N} b_{u_i}^{\nu} R_{u_i,z}^{\nu} \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu}} \right] \omega^{(z)}_{\nu}.
\]

After analysis of the matrix element \(\langle \phi_{\mu} | \hat{J}_{\nu}^2 | \phi_{\nu} \rangle\) one can conclude that this expression contains basically three types of integrals. Before, we demonstrate these integrals, for simplicity of notation let \(\{n_r^{\mu}\} \{n_s^{\nu}\}\) be the following one-dimensional overlap integral

\[
\langle \{n_r^{\mu}\} | \{n_s^{\nu}\} \rangle = \prod_{r=1}^{N} \left[ (z_r - R_{r,z}^{\mu})^{n_r^{\mu}} \right] \omega^{(z)}_{\nu} \prod_{s=1}^{N} \left[ (z_s - R_{s,z}^{\nu})^{n_s^{\nu}} \right] \omega^{(z)}_{\nu}.
\]
The first type of integral contains two coordinates \(\langle \phi_\mu^{(z)}|z_p,z_q|\phi_\nu^{(z)} \rangle\). Multiplying Eq.(D.5) by \(z_p\) and after application of relation (D.4) one obtains
\[
\langle \phi_\mu^{(z)}|z_p z_q|\phi_\nu^{(z)} \rangle = \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{sp} + \delta_{sq}\} + R_\nu^{\nu} \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{sp}\}
\]
\[
+ R_\nu^{\nu} \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{sq}\} + R_\nu^{\nu} R_\nu^{\nu} \{n_\nu^\mu\} \{n_\nu^\nu\}.
\]
(D.9)

The second type of integral contain a coordinate and the derivate with respect to a coordinate \(\langle \phi_\mu^{(z)}|z_q \partial_{z_i}|\phi_\nu^{(z)} \rangle\). Again, multiplying Eq.(D.5) by the \(z_q\) coordinate and after same manipulation the integral becomes
\[
\langle \phi_\mu^{(z)}|z_q \partial_{z_i}|\phi_\nu^{(z)} \rangle = n_\nu^\nu \{n_\nu^\mu\} \{n_\nu^\nu - \delta_{si} + \delta_{sq}\} + n_\nu^\nu R_\nu^{\nu} \{n_\nu^\mu\} \{n_\nu^\nu - \delta_{si}\}
\]
\[
- 2\alpha_\nu^\nu \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{si} + \delta_{si}\} - 2\alpha_i^\nu R_\nu^{\nu} \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{si}\}
\]
\[
- 2 \sum_{u=1}^{N} b_{ui} \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{su} + \delta_{su}\} - 2R_i^\nu \sum_{u=1}^{N} b_{ui} \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{su}\}
\]
\[
- 2 \sum_{u=1}^{N} b_{ui} R_i^\nu \{n_\nu^\mu\} \{n_\nu^\nu + \delta_{su}\} - 2R_i^\nu R_i^\nu \sum_{u=1}^{N} b_{ui} R_i^\nu \{n_\nu^\mu\} \{n_\nu^\nu\}.
\]
(D.10)

It should be noticed that the integral with a different order of the coordinate and the derivative, i.e., \(\langle \phi_\mu^{(z)}|\partial_{z_i} z_q|\phi_\nu^{(z)} \rangle\) can be transform to integral Eq.(D.10) by applying the commutation relation \([\partial_{z_i} z_q] = \delta_{iq}\). The last type of integral contains two derivatives. The general second derivatives are
\[
\frac{\partial}{\partial z_j} \frac{\partial}{\partial z_i} \phi_\nu^{(z)} = n_\nu^\nu (n_\nu^j - \delta_{ij}) \prod_{s=1}^{N} \left[(z_s - R_\nu^{\nu})n_\nu^s - \delta_{si} - \delta_{sj}\right] \omega_\nu^{(z)}
\]
\[
- 2n_\nu^\nu \left[\alpha_\nu^\nu (z_j - R_\nu^{\nu}) + \sum_{s=1}^{N} b_{sj} z_j \right] \prod_{s=1}^{N} \left[(z_s - R_\nu^{\nu})n_\nu^s - \delta_{si}\right] \omega_\nu^{(z)}
\]
\[
- 2(\alpha_\nu^\nu \delta_{ij} - b^{\nu}_{ij} z_j) \phi_\nu^{(z)}
\]
\[
- 2n_\nu^\nu \left[\alpha_\nu^\nu (z_i - R_\nu^{\nu}) + \sum_{s=1}^{N} b_{si} z_i \right] \prod_{s=1}^{N} \left[(z_s - R_\nu^{\nu})n_\nu^s - \delta_{si}\right] \omega_\nu^{(z)}
\]
\[
+ 4 \left[\alpha_\nu^\nu (z_i - R_\nu^{\nu}) + \sum_{s=1}^{N} b_{si} z_i \right] \left[\alpha_\nu^\nu (z_j - R_\nu^{\nu}) + \sum_{s=1}^{N} b_{sj} z_j \right] \omega_\nu^{(z)}.
\]
(D.11)
and the final form of the matrix element is equal to

\[
\langle \Phi^{(z)}_\mu | \frac{\partial}{\partial z_j} \frac{\partial}{\partial z_i} | \Phi^{(z)}_\nu \rangle = \\
n_i^\mu (n_j^\nu - \delta_{ij}) \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{si} - \delta_{sj}\} - 2n_i^\nu \alpha_j^\nu \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{si} + \delta_{sj}\} \rangle \\
- 2 \sum_{u=1}^{N} b_{uj} \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{si} + \delta_{su}\} \rangle - 2 \sum_{u=1}^{N} b_{uj} R_{u,z} \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{si}\} \rangle \\
- 2 (\alpha_i^\nu \delta_{ij} + b_{ij} R_{j,z}^\nu) \langle \{n_i^\mu\} | \{n_j^\nu\} \rangle - 2 b_{ij} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{si}\} \rangle \\
2n_j^\nu \alpha_i^\nu \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{sj} + \delta_{si}\} - 2n_j^\nu \sum_{u=1}^{N} \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{sj} + \delta_{su}\} \rangle \\
- 2n_j^\nu \sum_{u=1}^{N} b_{ui} R_{u,z} \langle \{n_i^\mu\} | \{n_j^\nu - \delta_{sj}\} \rangle + 4 \alpha_i^\nu \alpha_j^\nu \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{si} + \delta_{sj}\} \rangle \\
+ 4 \sum_{u=1}^{N} b_{ui} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{sj} + \delta_{su}\} \rangle + 4 \sum_{u=1}^{N} b_{ui} R_{u,z} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{si}\} \rangle \\
+ 4 \sum_{v=1}^{N} b_{vj} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{sv} + \delta_{si}\} \rangle + 4 \sum_{v=1}^{N} b_{vj} R_{v,z} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{si}\} \rangle \\
+ 4 \sum_{u=1}^{N} \sum_{v=1}^{N} b_{ui} b_{v,j} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{su} + \delta_{sv}\} \rangle \\
+ 4 \sum_{u=1}^{N} \sum_{v=1}^{N} b_{ui} b_{v,j} R_{u,z} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{sv}\} \rangle \\
+ 4 \sum_{u=1}^{N} \sum_{v=1}^{N} b_{ui} b_{v,j} R_{v,z} \langle \{n_i^\mu\} | \{n_j^\nu + \delta_{su}\} \rangle \\
+ 4 \sum_{u=1}^{N} \sum_{v=1}^{N} b_{ui} b_{v,j} R_{u,z} R_{v,z} \langle \{n_i^\mu\} | \{n_j^\nu\} \rangle. \tag{D.12}
\]

The matrix element for the \( \hat{J}_z \) operator

\[
\langle \Phi^{(z)}_\mu | \hat{J}_z | \Phi^{(z)}_\nu \rangle = -i \sum_{i=1}^{N} \langle \phi^{(z)}_\mu | \phi^{(z)}_\nu \rangle \times
\]

\[
\left[ \langle \phi^{(z)}_\mu | x_i | \phi^{(z)}_\nu \rangle \left( \frac{\partial}{\partial y_i} \right) \langle \phi^{(y)}_\mu | \phi^{(y)}_\nu \rangle - \langle \phi^{(y)}_\mu | y_i | \phi^{(y)}_\nu \rangle \left( \frac{\partial}{\partial x_i} \right) \langle \phi^{(z)}_\mu | \phi^{(z)}_\nu \rangle \right]. \tag{D.13}
\]

can be expressed in terms of the general overlap integral with the use of formula Eq.(D.6).
APPENDIX E

COMPUTER CODE

This Appendix is devoted to a discussion of the computer program which was used to obtain the numerical results presented in this dissertation. The integrals from the second Chapter were computationally implemented. Each integral, i.e. the overlap integral, the kinetic integral, the electron-nuclear attraction integral as well as the electron repulsion integral, were coded as independent subroutines. The correctness of each integral was checked by setting correlation parameters equal to zero and then comparing with integrals for Gaussian orbitals. Next, the numerical values for integrals over Gaussian geminals [53] were compared. In both cases the numerical values were the same. The preliminary calculations were performed for the helium atom and Li$^+$ cation. The energies in both cases were reproduced correctly. All preliminary calculations were performed on a Micro Vax machine, then the program was transferred to a CONVEX computer. Most of the calculations presented in this dissertation were obtained using this machine. Currently, a few versions of various programs for nonadiabatic calculations are available. The difference between versions is the optimization method used in calculations. There is a numerical optimization version, a version which contains first derivatives and finally a program with the Newton-Raphson method.

The organization of the program is the following. The main program initiates nonlinear parameters for the first energy calculation. After initiation the SUBROUTINE OPT initiates the optimization procedure. The nonadiabatic energy is calculated in SUBROUTINE ENERGY. This subroutine calls all subroutines where molecular integrals are evaluated. There are three different subroutines for molecular
integral evaluation: OVERLAP, KINET, TWOBODY. The two-step diagonalization procedure is used to find the energy value. For diagonalization the Jacobi method is used. For more extensive calculations the Jacobi procedure is replaced by the Ostrowski method. The last procedure calculates only the lowest eigenvalue and eigenvector. Finally, the numerical value of the functional is calculated in FUNCTION F.

The next part of this Appendix contains the code, an example of input and output.
PROGRAM NONADIABAT

C

********************************************************************
C * PROGRAMM NONADIABAT FOR ATOMIC AND MOLECULAR CALCULATION
C * USING EXPLICITLY CORRELATED GAUSSIAN-CLUSTER TYPE WAVEFUNCTION
C *
C * code written by
C *
C * Pawel M. KOZLOWSKI
C * DEPARTMENT OF CHEMISTRY
C * UNIVERSITY OF ARIZONA
C * TUCSON, AZ 85721.
C ********************************************************************

IMPLICIT REAL*8 (A-H,O-Z)
PARAMETER ( NOPTMAX=90 )
DIMENSION XGUESS(NOPTMAX)

C ***
C *** NOPTMAX IS MAXIMUM NUMBER OF OPTIMIZED PARAMETERS
C *** XGUESS IS INITIAL GUESS FOR NONLINEAR PARAMETERS
C ***
CALL INPUT(NOPT,XGUESS)
CALL OPT(NOPT,XGUESS)
STOP
END

C***************************************************************
C*******************************************************************

SUBROUTINE INPUT(NOPT,XGUESS)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION XGUESS(1)
DIMENSION XMM(5), Z(5), IAP(12,5), IBP(12,10), CSPIN(12)
COMMON /MOLPARAM/ N, M, IPER, xk, NP, XMM, Z, IAP, IBP
COMMON /SPIN/ CSPIN

C ***
READ(*,*) N
READ(*,*) M
READ(*,*) (XMM(I), I=1,N)
READ(*,*) (Z(I), I=1,N)
READ(*,*) xk
READ(*,*) IPER

C ***
DO 50 I=1,IPER
READ(*,*) (IAP(I,J), J=1,N)
50 CONTINUE
NP = N*(N-1)/2
DO 60 I=1,IPER
READ(*,*) (IBP(I,J), J=1,NP)
60 CONTINUE

C ***
READ(*,*) (CSPIN(I), I=1,IPER)

C ***
NOPT = M*N + M*N*(N-1)/2
READ(*,*) (XGUESS(I), I=1,NOPT)

C ***
WRITE(*,3)
3 FORMAT(' ', 80(IH-), /
WRITE(*,5)
5 FORMAT(' ', ' PROGRAM NONADAIABAT FOR MOLECULAR NONADIABATIC CALCULATION')
WRITE(*,6)
6 FORMAT(' ', ' WITH EXPLICITLY CORRELATED GAUSSIAN-CLUSTER')
TYPE WAVEFUNCTION', /)
WRITE(*,3)
WRITE(*,7)
7 FORMAT(' ', ' *** INPUT PARAMETERS ***',/ )
WRITE(*,9) N
9 FORMAT(' ', 'NUMBER OF PARTICLES N =', I3)
WRITE(*,11) M
11 FORMAT(' ', 'NUMBER OF GAUSSIAN CLUSTERS USED IN
EXPANSION M =', I4)
NLP = M*N + M*N*(N-1)/2
WRITE(*,13) NLP
13 FORMAT(' ', 'TOTAL NUMBER NONLINEAR PARAMETERS NLP =', I5,/) 
write(*,16)
16 FORMAT(' ', ' === MOLECULAR PARAMETERS ===',/ )
WRITE(*,18)
18 FORMAT(' ', 'PARTICLE MASSES CHARGE')
DO 20 I = 1, N
WRITE(*,24) I, XMM(I), Z(I)
20 CONTINUE
WRITE(*,3)
WRITE(*,29) xk
29 FORMAT(' ', '----- PARAMATR k = ',F12.6,/) 
WRITE(*,3)
WRITE(*,' ) PERMUTATIONS' 
WRITE(*,32) IPER
32 FORMAT(' ', /, ' TOTAL NUMBER OF PERMUTATIONS IPER =', I3, /)
WRITE(*,*) ' ORBITAL EXPONENTS PERMUTATIONS'
do 150 i=1,IPER
WRITE(*,155) (IAP(I,J), J=1,N)
155 FORMAT(6X, 8I5)
CONTINUE

WRITE(*,*) ' CORRELATION EXPONENTS PERMUTATIONS'
DO 160 I=1,IPER
WRITE(*,165) (IBP(I,J), J=1,NP)
160 CONTINUE

C ***
WRITE(*,*) ' SPIN-ADAPTATION COEFFICIENTS'
DO 170 1=1,IPER
WRITE(*,175) CSPIN(I)
170 CONTINUE

C ***
WRITE(*,3)
WRITE(*,*) OPTIMIZATION
WRITE(*,*) ' TOTAL NUMBER OF PARAMETERS NOPT = ', NOPT

WRITE(*,*) ' PARAMETERS FOR ORBITAL EXPONENTS '

MN = M*N
DO 80 I = 1, MN
WRITE(*,84) I, XGUESS(I)
84 FORMAT(8X,I3,8X,E12.6)
80 CONTINUE

WRITE(*,*) ' PARAMETERS FOR CORRELATION EXPONENTS '

NCORR = M*N*(N-1)/2
DO 90 I = 1, NCORR
WRITE(*,94) I, XGUESS(MN + I)
94 FORMAT(8X,I3,8X,E12.6)
90 CONTINUE

WRITE(*,3)
RETURN
SUBROUTINE OPT(NOPT,XGUESS)
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 NOISE
LOGICAL RESTART, EXACT
EXTERNAL F
DIMENSION XGUESS(l)

C ***
COMMON/T1/ND,NMAX,FFF,RR(90),DR(90),CURVE,ALPHA,NOISE,EXACT,
ALPH(90),RNOT(90),V(90,90),CURV(90),RESTART,JSTART,
FNOT,TIMLIM,TOLF,TOLR
K=-1
tolf = 1.d-04
tolr = 1.d-02
noise = 1.d-06
fff = 1.d+03
restart = .false.
nd = NOPT
C *** NOPT = NUMBER OF OPTIMIZED PARAMETERS
C *** INITIAL PARAMETERS
DO 1212 I = 1, ND
RR(I) = XGUESS(I)
1212 CONTINUE
C ***
CALL TRUDGE(K,f)
66 CONTINUE
RETURN
end
FUNCTION f(in)
implicit real*8 (a-h,o-z)
C ***
PARAMETER ( Nmax = 5 )
PARAMETER ( NPmax = Nmax*(Nmax-1)/2 )
PARAMETER ( Mmax = 100 )
PARAMETER ( NAA = Mmax*Nmax )
PARAMETER ( NBB = Mmax*Nmax*(Nmax-1)/2 )
PARAMETER ( MM = Mmax*Mmax )

C ***
DIMENSION A(NAA), B(NBB), C(MMAX), R2(NPMAX)
DIMENSION P(25)

C ***
COMMON /t1/nd, ndmax, fff, rr(00)
COMMON /MOLPARAM/ N, M, IPER, xk
COMMON /FFF/ VEC(MM), SSQ(Mmax,Mmax), S(Mmax,Mmax), TCM(Mmax,Mmax)
COMMON /MIN/ FMIN, LOOKS
DATA P/2,3,5,7,11,13,17,19,23,29,31,37,41,43,
47,53,59,61,67,71,73,79,83,89,97/

C***************************************************
C *** GENERATION OF ORBITAL EXPONENTS
MN = M*N
DO 35 J = 1, MN
   A(J) = rr(J)
35 CONTINUE

C***************************************************
C *** GENERATION OF CORRELATION EXPONENTS
MNP = M*N*(N-1)/2
DO 40 I = 1, MNP
   B(I) = rr(MN + I)
40 CONTINUE

CALL ENERGY(A,B,EMIN,KLM)
IF(KLM.EQ.5) THEN
    FUN = EMIN*LOOKS
    GOTO 6666
ELSE
    SSS=0.0D+00
    TTT=0.0D+00
END IF

C ***
DO 394 JJ=1,M
    wxx = 0.0d+00
DO 1001 I=1,M
    wxx = wxx + VEC(I)*SSQ(I,JJ)
1001 CONTINUE
C(JJ) = wxx
394 CONTINUE

DO 90 L=1,M
    DO 90 K=1,M
    SSS = SSS + C(L)*C(K)*S(L,K)
    TTT = TTT + C(L)*C(K)*TCM(L,K)
90 CONTINUE

C ***
FUN = EMIN + xk*TTT/SSS
FF = FUN
IF(FF.GT.FMIN) GO TO 8888
WRITE(*,*)'NORMALIZATION = ', SSS
WRITE(*,*)'ENERGY = ', EMIN
WRITE(*,*)'TCM = ', TTT
WRITE(*,*)'J[k] = ', FF
WRITE(*,*)'******************************************************************************'
WRITE(*,*)'EXPANSION COEFFICIENTS'
WRITE(*,*)'============================================================================='
DO 33 J = 1, M
WRITE(*,698) J, C(J)
698 FORMAT(10X, 'C(', I2, ') =' D17.10)
33 CONTINUE
C ***
WRITE(*,*) '******************************************************************************
WRITE(*,*) ' NONLINEAR PARAMETERS'
WRITE(*,*) '******************************************************************************
DO 66 I=1, nd
WRITE(*,648) I, rr(I)
648 FORMAT(10X, 'rr(', I2, ') =' D17.10)
66 continue
C ***
6666 CONTINUE
8888 fff = FUN
    f = fff
    return
end    *
C******************************************************************************
SUBROUTINE ENERGY(A,B,EMIN,KLM)
IMPLICIT REAL*8 (A-H,O-Z)
C ***
C *** N IS NUMBER OF PARTICLES
C *** M IS NUMBER OF FUNCTIONS USED IN EXPANSION
C *** IPER IS NUMBER OF PERMUTATIONS
C *** NP = N*(N-1)/2 IS NUMBER OF INTERACTING PAIRS
C *** MN = M*N IS NUMBER OF ORBITAL EXPONENTS
C *** MNP = M*N*(N-1)/2 IS NUMBER OF CORRELATION EXPONENTS
C ***
PARAMETER ( Nmax = 5 )
PARAMETER ( Mmax = 100 )
PARAMETER ( IPmax = 12)
PARAMETER ( NPmax = Nmax*(Nmax-1)/2 )
PARAMETER ( MNmax = Mmax*Nmax )
PARAMETER ( MNPmax = Mmax*Nmax*(Nmax-1)/2 )
PARAMETER ( MTR = Mmax*(Mmax+1)/2 )
PARAMETER ( MM = Mmax*Mmax )

C ***

DIMENSION A(l), B(l),
    alphaL(Nmax), alphaK(Nmax), betaL(NPmax), betaK(NPmax),
    OVPER(IPmax), TPER(IPmax),
    TCMPER(IPmax), VVPER(IPmax),
    S(Mmax,Mmax), H(Mmax,Mmax), SNORM(Mmax,Mmax),
    TCM(Mmax,Mmax), SSQ(Mmax,Mmax), f(MTR), vec(MM),
    T(Mmax,Mmax), VNE(Mmax,Mmax), VEE(Mmax,Mmax)

C ***

COMMON /MOLPARAM/ N, M, IPER, xk, NP, XMM(5), Z(5),
    IAP(12,5), IBP(12,10)
COMMON /FFF/ VEC, SSQ, S, TCM
COMMON /SPIN/ CSPIN(12)
COMMON /NORM/ SNORM

C *** LOOP OVER CLUSTER FUNCTIONS

DO 333 L=M
  DO 333 K=M
    KLM = 1

C *** PARAMETERS FOR K-th CLUSTER FUNCTION

DO 110 II = 1, N
  alphaK(II) = 0.0d+00
  alphaK(II) = A( N*(K-1) + IAP(1,II) )
  CONTINUE
do 112 II = 1, NP  
   betaK(II) = B( NP*(K-1) + IBP(1,II) )  
112 CONTINUE

C *** PARAMETERS FOR L-th CLUSTER FUNCTION WITH PERMUTATIONS

   do 200 JJ = 1, IPER  
       DO 210 II = 1, N  
          alphaL(II) = 0.0d+00  
          alphaL(II) = A( N*(L-1) + IAP(JJ,II) )  
210 CONTINUE  
   do 212 II = 1, NP  
       betaL(II) = 0.0d+00  
       betaL(II) = B( NP*(L-1) + IBP(JJ,II) )  
212 CONTINUE

   CALL OVERLAP(N, alphaL, betaL, alphaK, betaK, OVPER(JJ), KLM)  
   IF(KLM.EQ.5) GO TO 1414  
   CALL KINET(alphaL, alphaK, OVPER(JJ), TPER(JJ), TCMPER(JJ))  
   CALL TWOBODY(alphaL, alphaK, VVPER(JJ), KLM)  
   IF(KLM.EQ.5) GO TO 1414  
200 CONTINUE

C

C *** SPIN-ADAPTED MATRIX ELEMENTS

C

SSSS = 0.0D+00  
TTCC = 0.0D+00  
HHHHH = 0.0D+00  
DO 5010 IM = 1, IPER  
SSSS = SSSS + CSPIN(IM)*OVPER(IM)  
TTCC = TTCC + CSPIN(IM)*TCMPER(IM)  
HHHHH = HHHHH + CSPIN(IM)*( TPER(IM) + VVPER(IM) )  
5010 CONTINUE

S(L,K) = SSSS
TCM(L,K) = TTCC
H(L,K) = HHHH
S(K,L) = S(L,K)
TCM(K,L) = TCM(L,K)
H(K,L) = H(L,K)

333 CONTINUE

C ***
C *** NORMALIZATION
C ***

write(*, *) ' overlap'
call tab(S,M,M,MMAX,MMAX)
write(*, *) ' hamiltonian'
call tab(H,M,M,MMAX,MMAX)
DO 58 I=1,M
DO 58 J=1,M
SNORM(I,J) = S(I,J)

58 CONTINUE
DO 59 I=1,M
DO 59 J=1,M
S(I,J) = S(I,J)/(DSQRT(SNORM(I,I))*DSQRT(SNORM(J,J)))
H(I,J) = H(I,J)/(DSQRT(SNORM(I,I))*DSQRT(SNORM(J,J)))
TCM(I,J) = TCM(I,J)/(DSQRT(SNORM(I,I))*DSQRT(SNORM(J,J)))

59 CONTINUE
C call tab(S,M,M,MMAX,MMAX)
C call tab(H,M,M,MMAX,MMAX)

C**************************************************************************************************
C*                                              *
C*                                              *
C*                  HC = SCE                      *
C*                                              *
C*                                              *
C*                                              *
C*                                              *
C*                                              *
C**************************************************
call diagon(S,M,f,VEC)
do 1000 i = 1,M
do 1000 j = 1,M
T(i,j) = 6.0d0+00
1000 continue
do 1004 i=1,M
ii = i * (i + 1)/2
IF(f(ii).LT.1.0D-12) go to 1414
T(i,i) = 1.0d+00/DSQRT(f(ii))
1004 continue
C.....MATRIX S**(1/2)
DO 1010 I = 1, M
DO 1010 J = 1, M
QQ = 0.0D+00
do 1015 Ip=1,M
do 1015 Jq=1,M
QQ = QQ + VEC(I+(Ip-1)*M)*T(Ip,Jq)*VEC(J+(Jq-1)*M)
1015 continue
Vne(I,J) = QQ
1010 continue
DO 779 IC=1,M
DO 779 JC=1,M
SSQ(IC,JC) = Vne(IC,JC)
779 continue
DO 2010 I = 1, M
DO 2010 J = 1, M
WW = 0.0D+00
do 2015 ii=1,M
do 2015 jj=1,M
WW = WW + Vne(I,ii)*H(ii,jj)*Vne(jj,J)
2015  continue
Vec(I,J) = WW
2010  continue
CALL diagon(Vec,M,I,vec)
do 300 I=1,M
do 300 J=1,M
xx = 0.0D+00
do 303 Ip=1,M
xx = xx + vec(Ip + (J-1)*M)*vec(Ip + (I-1)*M)
303  continue
T(I,J) = xx
300  continue
DO 4010 I = 1, M
DO 4010 J = 1, M
Vne(I,J) = 0.0D+00
QQ = 0.0D+00
do 4015 Ip=1,M
do 4015 Jq=1,M
QQ = QQ + VEC(Ip+(I-1)*M)*Vee(Ip,Jq)*VEC(Jq+(J-1)*M)
4015  continue
Vne(I,J) = QQ
4010  continue
C---
EMIN = f(1)
iii = 1
do 739 i=1,M
ii = i*(i+1)/2
IF(f(iii).L.T.EMIN) then
EMIN=f(iii)
iii = i
endif
739  continue
    do 1313 j=1,M
       vec(j) = vec(M*(ii-1)+j)
1313  CONTINUE
    GO TO 1515
1414  EMIN = 10.0D-00
1515  RETURN
END

SUBROUTINE DIAGON(HHH,n,f,vec)
    implicit real*8 (a-h,o-z)

C ***
PARAMETER ( Mmax = 100 )
PARAMETER ( MTR = Mmax*(Mmax+1)/2 )
PARAMETER ( MM = Mmax*Mmax )
C ***
DIMENSION HHH(Mmax,Mmax), f(MTR), vec(MM),
      a(Mmax), jb(Mmax)
C ***
C.....TRANSFORMATION
C ***
nn = n * (n+1) / 2
   ii = 0
   do 1001 i = 1,n
      do 1001 j = 1,i
         ii = ii + 1
         f(ii) = HHH(i,j)
1001  continue
    call yacobi (f,vec,n,nn,a,jb)
    return
end

SUBROUTINE YACOBI (A,U,N,NNP1D2,BIG,JB)
C L(I)=(I*(I-1))/2
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(NNP1D2),U(N*N),BIG(N),JB(N)
DATA ZERO/0.D00/
DATA EPS/1.D-14/
DATA ONE/1.D00/
c ABS(X)=DABS(X)
c SQRT(X)=DSQRT(X)
L(I)=(I*(I-1))/2
C ***
c WRITE(6,*')YACOBI: N,NNP1D2', N,NNP1D2
U(I)=ONE
IF (N.EQ.1) GO TO 999
J=0
K=0
N2=N*N
DO 10 I=1,N2
10 U(I)=ZERO
DO 30 I=1,N
J=J+I
JJ=K+I
K=K+N
U(JJ)=ONE
C SECTION TO LOCATE BIGGEST OFF-DIAGONAL ELEMENT IN ROW I
15 IM1=I-1
IF (IM1.EQ.0) GO TO 30
16 BIG(I)=ZERO
DO 20 JJ=1,IM1
1J=L(I)+JJ
B=ABS(A(IJ))
IF (B.LE.BIG(I)) GO TO 20
18 BIG(I) = B
   JB(I) = JJ
20 CONTINUE
30 CONTINUE
C  LOCATE ROTATION PIVOT
31 CONTINUE
   IBIG = 2
   DO 35 I = 2, N
      IF (BIG(I) .GT. BIG(IBIG)) IBIG = I
35 CONTINUE
   BIGGST = BIG(IBIG)
   JBIG = JB(IBIG)
   IF (BIGGST .LE. EPS) GO TO 999
C  BEGIN ROTATION
40 II = L(IBIG) + IBIG
   IJ = L(IBIG) + JBIG
   JJ = L(JBIG) + JBIG
   AB = A(II) - A(JJ)
   AA = A(IJ) + A(IJ)
   D = SQRT(AB * AB + AA * AA)
   IF (AB .LT. ZERO) D = -D
   T = AA / (AB + D)
   TSQ = T * T
   CSQ = ONE / (ONE + TSQ)
   C = SQRT(CSQ)
   S = C * T
   AB = AA * T
   D = (A(II) + AB + TSQ * A(JJ)) * CSQ
   A(JJ) = (A(JJ) - AB + TSQ * A(II)) * CSQ
   A(II) = D
   A(IJ) = ZERO
III=4
KIX=(IBIG-1)*N
KJX=(JBIG-1)*N
DO 60 I=1,N
KI=KIX+I
KJ=KJX+I
D=C*U(KI)+S*U(KJ)
U(KJ)=C*U(KJ)-S*U(KI)
U(KI)=D
IF (I-JBIG) 45,54,46
45 KJ=L(JBIG)+I
KI=L(IBIG)+I
GO TO 50
46 KJ=L(I)+JBIG
IF (I-JBIG) 47,55,48
47 KI=L(IBIG)+I
III=2
IF (JB(I).EQ.JBIG) III=3
GO TO 50
48 KI=L(I)+IBIG
III=1
IF (JB(I).EQ.IBIG. OR JB(I).EQ.JBIG) III=3
50 D=C*A(KI)+S*A(KJ)
A(KJ)=C*A(KJ)-S*A(KI)
A(KI)=D
GO TO (51,52,55,60),III
51 B=ABS(A(KI))
IF (B.LE.BIG(I)) GO TO 52
BIG(I)=B
JB(I)=IBIG
52 B=ABS(A(KJ))
IF (B.LE.BIG(I)) GO TO 60

53  BIG(I)=B
    JB(I)=JBIG
    GO TO 60

54  IF (I.EQ.1) GO TO 60

55  IM1=I-1
    BIG(I)=ZERO
    DO 58  J=1,IM1
    IJ=L(I)+J
    B=ABS(A(IJ))
    IF (B.LE.BIG(I)) GO TO 58
    BIG(I)=B
    JB(I)=J

58  CONTINUE
60  CONTINUE

C    END OF ROTATION
    GO TO 31

999 CONTINUE

C LOCK EIGENVECTORS SO THAT FIRST COEFFICIENT IS ALWAYS
C POSITIVE.

IJ=1
    DO 501  I=1,N
    IF (U(IJ).GE.ZERO) GO TO 503
    DO 502  J=1,N
    U(IJ+J-1)=-U(IJ+J-1)

502  CONTINUE
503  IJ=IJ+N
501  CONTINUE

RETURN
END

C**************************************************************************************
SUBROUTINE OVERLAP(N,alphaL,betaL,alphaK,betaK,OV,KLM)

C ***
IMPLICIT REAL*8 (A-H,O-Z)
PARAMETER ( Nmax=5 )
DIMENSION alphaL(1), alphaK(1),
       betaL(1), betaK(1)
DIMENSION BL(Nmax,Nmax), BK(Nmax,Nmax),
       AB(Nmax,Nmax), FAC(Nmax,Nmax), IPVT(Nmax)
COMMON/BLBK/ BL, BK, AB, DETAB
DATA pi/3.1415926535898D00/
    XN = 1.5d+00*N    
    PI = pi**XN

C *** SUBROUTINE OVERLAP CALCULATES OVERLAPES INTEGRALS
C *** FOR UN-NORMALIZED GAUSSIAN CLUSTERS /N - NUMBER OF PARTICLES/
C ***

C------------------------
C    TRANSFORMATION
C------------------------
DO 10 I = 1, N
    DO 10 J = 1, N
    BL(I,J) = 0.0D+00
    BK(I,J) = 0.0D+00
    AB(I,J) = 0.0D+00
10 CONTINUE
II = 0
DO 20 I = 1, N-1
    DO 20 J = I+1, N
    II = II + 1
    BL(I,J) = - betaL(II)
    BK(I,J) = - betaK(II)
\begin{verbatim}
BL(J,I) = BL(I,J)
BK(J,I) = BK(I,J)

20 CONTINUE
DO 28 JJ = 1, N
  S1 = 0.0D+00
  S2 = 0.0D+00
  DO 25 II = 1, N
    S1 = S1 + BL(JJ,II)
    S2 = S2 + BK(JJ,II)
  25 CONTINUE
BL(JJ,JJ) = -S1
BK(JJ,JJ) = -S2

28 CONTINUE

C------------------------
C CONSTRUCTION OF MATRIX AB
C------------------------

DO 30 I=1,N
  DO 30 J=1,N
    AB(I,J) = BL(I,J) + BK(I,J)
  30 CONTINUE

DO 35 II=I,N
  AB(II,II) = AB(II,II) + alphaL(II) + alphaK(II)
  35 CONTINUE

C ***
C *** det(A + B) = DETAB
C *** OVERLAP INTEGRAL = OV
C ***
CALL DLFTRG(N,AB,Nmax,FAC,Nmax,IPVT)
CALL DLFDRG(N,FAC,Nmax,IPVT,DETI,DET2)
DETAI3 = DET1*10.0**DET2
IF(DETAB.LE.0.0D+00) GO TO 300
\end{verbatim}
OV = PIFAC / ( DETAB*DSQRT(DETAB) )

C ***
C WRITE(*,*) ' ALPHAL, ALPHAK ' 
C DO 3 I =1, N 
C WRITE(*,*) ALPHAL(I), ALPHAK(I) 
C3 CONTINUE 
C WRITE(*,*) OV 
C
GO TO 500 
300 KLM = 5 
500 RETURN 
END

C********************************************************************
C********************************************************************
SUBROUTINE I<:INET(alphaL,alphak,OV,Tlk,TCMlk)
IMPLICIT rea!8 (a-h, o-z)
C***
DIMENSION alphaL(l), alphaK(l)
PARAMETER ( Nmax=5 )
DIMENSION SIijlk(Nmax,Nmax), delta(Nmax,Nmax)
C***
COMIVION IrvIOLPARAMI N, lvI, IPER, xk, NP, XMM(5), Z(5)
COMIVION II3LI3KI I3L(Nmax, Nmax), BK(Nmax,Nmax), AB(Nmax,Nmax), DETAB
C-----------------------
C***
X VECTOR(N) MATRIX WITH MASS OF PARTICLES
C***
XM - SUM OF MESSES
XM = 0.0D+00
DO 4 I = 1, N 
XM = XM + XMM(I) 
4 CONTINUE
C *** Tlk - PARTICLE KINETIC ENERGY INTEGRAL

C *** TCMlk - CENTER OF MASS MOTION KINETIC ENERGY INTEGRAL

    Tlk = 0.0D+00
    TCMlk = 0.0D+00

C *** KRONECER DELTA

    do 10 id=1,N
    do 10 jd=1,N
    delta(id,jd) = 0.0D+00

10 continue

    do 20 ii=1,N
    delta(ii,ii) = 1.0D+00

20 continue

C ***

    Do 1000 i=1,N
    Do 1000 j=i,N
    SSS = 0.0D+00

C ***

    do 80 Im=1,N
    do 80 Is=1,N
    call Jpq11(N,Im,Is,ww)
    SSS = SSS + (delta(Im,i)*alphaL(Im) + bL(i,Im))*
          (delta(Is,j)*alphaK(Is) + bK(j,Is))*ww

80 continue

    Slijlk(i,j) = 6.0d+00*OV*(1.0d+00/DETAB)*SSS
    Slijlk(j,i) = Slijlk(i,j)

1000 CONTINUE

C ***

    DO 400 I=1,N
    Tlk = Tlk + Slijlk(I,I)/XMM(I)

400 CONTINUE
Tk = 0.5d+00*Tk

C ***
DO 500 I=1,N
DO 500 J=1,N
TCMlk = TCMlk + Siijkl(I,J)
500 CONTINUE
TCMlk = 0.5d+00*TCMlk/XM
return
end

C********************************************************************
SUBROUTINE Jpq11(N,Ip,Iq,Xbpq)
IMPLICIT real*8 (a-h, o-z)
C ***
PARAMETER ( Nmax=5 )
DIMENSION dd(Nmax,Nmax), FAC(Nmax,Nmax), IPVT(Nmax)
C ***
COMMON/BLBK/ BL(Nmax,Nmax), BK(Nmax,Nmax),
AB(Nmax,Nmax), DETAB

C subroutine Jpq11 calculates the derivative
C bpqlk det(A + B)

C-----------------------
do 7 i = 1,N
do 7 j = 1,N
dd(i,j) = 0.0D+00
dd(i,j) = AB(i,j)
7 continue
C---
C.....derivative with respect to b pq
C---
do 30 l=1,N
dd(Ip,I) = 0.0D+00
dd(I,Iq) = 0.0D+00

continue

dd(Ip,Iq) = 1.0D+00

CALL DLFTRG(N,dd,Nmax,FAC,Nmax,IPVT)
CALL DLFDRG(N,FAC,Nmax,IPVT,DET1,DET2)

Xbpq = DET1*10.0**DET2
RETURN
END

C************************************************************
C************************************************************
SUBROUTINE TWOBODY(alphaL, alphaK, VV, KLM)
IMPLICIT real*8 (a-h, o-z)
C
***
PARAMETER ( Nmax = 5 )
PARAMETER ( IRED = Nmax - 2 )
PARAMETER ( NPmax = Nmax*(Nmax - 1)/2 )
DIMENSION alphaL(1), alphaK(1)
DIMENSION IN1(3), IN2(6), IN3(6), IN4(10), IN5(10), IN6(10)
DIMENSION DDij(Nmax,Nmax),
IND(NPmax,NPmax,IRED,IRED),
BRED(Nmax,Nmax,IRED),
VVV(Nmax,Nmax),
FAC(Nmax,Nmax), IPVT(Nmax)
C ***
COMMON /MOLPARAM/ N, M, IPER, xk, NP, XMM(5), Z(5)
COMMON/BLBK/ BL(Nmax,Nmax), BK(Nmax,Nmax),
AB(Nmax,Nmax), DETAB
DATA PI/3.1415926535898D0/
XP = 2.5 + 1.5*(N-2.0)
PIFAC = 2.0D+00*PI**XP
C ***
DATA IN1/3,2,1/
DATA IN2/3,2,1,1,1/
DATA IN3/4,4,3,4,3,2/
DATA IN4/3,2,2,1,1,1,1,1,1,1,1,1,1/
DATA IN5/4,4,3,3,4,3,2,2,2/
DATA IN6/5,5,4,5,4,5,4,5,4,4,4,3/
C ***
IND(1,2,1,1) = IN1(I)
IND(1,3,1,1) = IN1(2)
IND(2,3,1,1) = IN1(3)
C ***
II = 0
DO 5 I = 1, 3
 DO 5 J = I+1, 4
 II = II + 1
IND(I,J,1,2) = IN2(II)
IND(I,J,2,2) = IN3(II)
5 CONTINUE
C ***
II = 0
DO 10 I = 1, 4
 DO 10 J = I+1, 5
 II = II + 1
IND(I,J,1,3) = IN4(II)
IND(I,J,2,3) = IN5(II)
IND(I,J,3,3) = IN6(II)
10 CONTINUE
KLM = 1
C-----------------------
C ***
C *** Subroutine TWOBODY calculates TWO-BODY INTERACTION INTEGRALS
C *** for unnormalized Gaussians clusters
C ***
C----------------------------------------------------
C----------------------------------------------------
IF(N.GT.2) GO TO 333
Dij = AB(1,1)*AB(2,2) - AB(1,2)*AB(2,1)
VINT = 1.0d+00/(Dij*DSQRT(AB(1,1) + AB(2,2) + 2.0d+00*AB(1,2))
C
C *** MATRIX ELEMENT iwl—1/r 12—wkj
C
VV = Z(1)*Z(2)*PIFAC*VINT
GO TO 500
C ***
333  NRED = N - 2
    Vij = 0.0d+00
    DO 1000 i=1, N-1
    DO 1000 j=i+1,N
C
C ---i,REDUCTIONj---
C
C    DO 30 lw=1,N
    DO 30 Jw=1,N
    DDij(lw,Jw) = 0.0d+00
    DDij(lw,Jw) = AB(lw,Jw)
30    CONTINUE
C.....
C.....det(A + B;i,j)
C.....
    DO 40 lz=1,N
DDij(i,Iz) = 0.0d+00
DDij(Iz,i) = 0.0d+00
DDij(j,Iz) = 0.0d+00
DDij(Iz,j) = 0.0d+00

continue

DDij(i,i) = 1.0d+00
DDij(j,j) = 1.0d+00

CALL DLFTRG(N,DDij,Nmax,FAC,Nmax,IPVT)
CALL DLFDRG(N,FAC,Nmax,IPVT,DET1,DET2)

DETABij = DET1*10.0**DET2
IF(DETABij.LE.0.0d+00) GO TO 300

C ***
C.....FIRST REDUCTION
C ***

KK = IND(i,j,1,NRED)
DRED1 = AB(KK,KK)

DO 60 In=1,N
  DO 60 Im=1,N
  BRED(In,Im,1) = (bL(In,Im) + bK(In,Im)) -
                 (1.0d+00/DRED1)*(bL(In,KK) + bK(In,KK))*(bL(Im,KK) + bK(Im,KK))

60  CONTINUE

IF(NRED.EQ.1) GO TO 5000

C ***
C.....SECOND REDUCTION
C ***

LL = IND(i,j,2,NRED)
DRED2 = AB(KK,KK)*AB(LL,LL) - AB(KK,LL)*AB(LL,KK)

DO 80 In=1,N
  DO 80 Im=1,N
  BRED(In,Im,2) = BRED(In,Im,1) -
                 (DRED1/DRED2)*BRED(In,LL,1)*BRED(Im,LL,1)
CONTINUE

IF(NRED.EQ.2) GO TO 5000

C ***
C.....THIRD REDUCTION
C ***

MM = IND(i,j,3,NRED)

DRED3 = AB(KK,KK)*AB(LL,LL)*AB(MM,MM)
+ AB(LL,KK)*AB(MM,LL)*AB(KK,MM)
   + AB(MM,KK)*AB(KK,LL)*AB(LL,MM)
   - AB(MM,KK)*AB(LL,LL)*AB(KK,MM)
   - AB(KK,KK)*AB(MM,LL)*AB(LL,MM)
   - AB(LL,KK)*AB(KK,LL)*AB(MM,MM)

DO 100 Im=1,N
   DO 100 Im=1,N
   BRED(In,Im,3) = BRED(In,Im,2) -
   (DRED2/DRED3)*BRED(In,MM,2)*BRED(Im,MM,2)
100 CONTINUE

5000 CONTINUE

Di = alphaL(i) + alphaK(i) + BRED(i,i,NRED)
Dj = alphaL(j) + alphaK(j) + BRED(j,j,NRED)
Dij = Di*Dj - BRED(i,j,NRED)*BRED(j,i,NRED)

VVV(i,j) = (1.0d+00/(DETABij*DSQRT(DETABij)))*
           (1.0d+00/(Dij*DSQRT(Di + Dj + 2.0d+00*BRED(i,j,NRED)))))

C *** MATRIX ELEMENT \|wi—1/rij—wk\|

C

Vij = Vij + Z(i)*Z(j)*VVV(i,j)

1000 CONTINUE

VV = PIFAC*Vij

C ***

GO TO 500
300  KLM = 5
500  RETURN
END

C**************************************************************************************
C**************************************************************************************
SUBROUTINE DISTANCE(A,B,C,I,J,IDD,RR2)

IMPLICIT REAL*8 (A-H,O-Z)

C***
PARAMETER ( Nmax = 5 )
PARAMETER ( Mmax = 100 )
PARAMETER ( NPmax = Nmax*(Nmax-1)/2 )
C***

C***

DIMENSION A(1), B(1), C(1),
   alphaL(Nmax), alphaK(Nmax),
   betaL(NPmax), betaK(NPmax),
   OVPP(12,12),
   S(Mmax,Mmax), RDIs(Mmax,Mmax),
   GOVALP(NMAX), GOVBET(NPmax)

C***

COMMON /MOLPARAM/ N, M, IPER, xk, NP, XMM(5), Z(5),
   IAP(12,5), IBP(12,10)
COMMON /SPIN/ CSPIN(12)
COMMON /NORM/ SNORM(Mmax,Mmax)

C***

C*** LOOP OVER CLUSTER FUNCTIONS
C***

DO 333 L=1,M
   DO 333 K=1,M
      SSSS = 0.0D+00
      SSRR = 0.0D+00
   333 CONTINUE

DO 200 JJ1 = 1, IPER
   DO 200 JJ2 = 1, IPER
   C ***
   C *** PARAMETERS FOR L-th CLUSTER FUNCTION
   C ***
   DO 210 II = 1, N
      alphaL(II) = 0.0d+00
      alphaL(II) = A( N*(L-1) + IAP(JJ1,II) )
   210 CONTINUE
   DO 212 II = 1, NP
      betaL(II) = 0.0d+00
      betaL(II) = B( NP*(L-1) + IBP(JJ1,II) )
   212 CONTINUE
   C ***
   C *** PARAMETERS FOR K-th CLUSTER FUNCTION
   C ***
   DO 110 II = 1, N
      alphaK(II) = 0.0d+00
      alphaK(II) = A( N*(K-1) + IAP(JJ2,II) )
   110 CONTINUE
   DO 112 II = 1, NP
      betaK(II) = 0.0d+00
      betaK(II) = B( NP*(K-1) + IBP(JJ2,II) )
   112 CONTINUE
   CALL OVERLAP(N, alphaL, betaL, alphaK, betaK, OVPP(JJ1, JJ2), KL.M)
   CALL GROVER(N, alphaL, betaL, alphaK, betaK, OVPP(JJ1, JJ2), GOVALP, GOVBET)
   SSSS = SSSS + CSPIN(JJ1)*CSPIN(JJ2)*OVPP(JJ1, JJ2)
   SSRR = SSRR - CSPIN(JJ1)*CSPIN(JJ2)*GOVBET(1DD)
   200 CONTINUE
   S(L,K) = SSSS
RDIS(L,K) = SSRR

333 CONTINUE

C ***

C *** NORMALIZATION

C ***

DO 59 IW=1,M
DO 59 JW=1,M
S(IW,JW) = S(IW,JW)/(DSQRT(SNORM(IW,IW))*DSQRT(SNORM(JW,JW)))
RDIS(IW,JW) =
RDIS(IW,JW)/(DSQRT(SNORM(IW,IW))*DSQRT(SNORM(JW,JW)))

59 CONTINUE

SUM1 = 0.0D+00
SUM2 = 0.0D+00
DO 99 L = 1, M
DO 99 K = 1, M
SUM1 = SUM1 + C(L)*C(K)*RDIS(L,K)
SUM2 = SUM2 + C(L)*C(K)*S(L,K)

99 CONTINUE

RR2 = SUM1/SUM2
RETURN
END

C*************************************************************************************************************************

SUBROUTINE SEARCH(LEAVE,GAUSS)
IMPLICIT REAL*(A-H,O-Z)

C

C SUBROUTINE LOCATES A LOCAL MINIMUM ALONG A GIVEN ONE-DIMENSIONAL

C SEARCH DIRECTION.

C F(ALF) = FUNC(X+ALF*DX) FIND OPTIMUM ALF VALUE.

C LOOKMAX = MAXIMUM NUMBER OF FUNCTION EVALUATIONS BEFORE SEARCH IS

C TERMINATED

C ENTER SUBROUTINE WITH FOLLOWING
C N = DIMENSIONALITY OF X SPACE
C X = INITIAL POSITION (IN N DIMENSIONAL PARAMETER SPACE)
C FUNC = F(0), I.E. FUNCTION VALUE AT INITIAL X.
C DX = SEARCH DIRECTIONS (IN N-DIMENSIONAL SPACE)
C AMIN = ESTIMATED INITIAL STEP SIZE
C NOISE = ACCURACY OF FUNC VALUES. VARIATIONS SMALLER THAN NOISE
C ARE NOT CONSIDERED TO BE SIGNIFICANT.
C EXACT = .FALSE. SUPPRESSES FINAL CHECK OF QUADRATIC FIT.
C
C EXIT FROM SUBROUTINE WITH FOLLOWING
C X = CALCULATED MINIMUM
C FUNC = F(AMIN), I.E. FUNCTION VALUE AT FINAL X.
C CURVE = CALCULATED CURVATURE ALONG SEARCH DIRECTIONS
C LEAVE = 0 IF NORMAL EXIT
C .  = 2 IF EXCESSIVE NUMBER OF FUNCTIONS EVALUATIONS
C
C N, NMAX, FUNC, AND X ARE SHARED WITH SUBROUTINE GAUSS.
C ALL VARIABLES IN COMMON T1 ARE SHARED WITH PROGRAM CALLING SEARCH
C
COMMON/T1/ N, NMAX, FF, X(90), DX(90), CURVE, AMIN, NOISE, EXACT
COMMON/MIN/ FMIN, LOOKS

DIMENSION XNOT(90), F(9), SET(9)
EQUIVALENCE (F(1),F1),(F(3),F3),(F(4),F4),(F(5),F5),(F(6),F6),
1 (F(7),F7),(F(9),F9),(SET(1),SET1),
2 (SET(2),SET2),(SET(3),SET3),(SET(4),SET4),(SET(5),SET5),
3 (SET(6),SET6),(SET(7),SET7),(SET(8),SET8),(SET(9),SET9)
LOGICAL BACK, SET, SET1, SET2, SET3, SET4, SET5, SET6, SET7, SET8, SET9
1, EXACT, HOLD
LOGICAL AIF
REAL NOISE
LOOKS=0
LEAVE = 0
LOOKMAX=30
DO 5 I=1,N
5 XNOT(I)=X(I)
   ALF=AMIN
   AMIN=0.D+00
   FNOT = Fff
   FMIN=Fff
   FNEXT=1.0D+30
   IR=4
10 LOOKS=LOOKS+1
   IF(LOOKS.LE.LOOKMAX) GO TO 20
   LEAVE=2
   WRITE(6,13) LOOKS
13 FORMAT(/' EXCESSIVE NUMBER OF FUNCTION EVALUATIONS =',I3/)
   C
   C   RETURN FROM SUBROUTINE
   C
15 DO 16 I=1,N
16 X(I)=XNOT(I)+AMIN*DX(I)
   Fff=FMIN
   RETURN
   C
   C   EVALUATE F(ALF)=FUNC(XNOT+ALF*DX)
   C
20 DO 25 I=1,N
25 X(I)=XNOT(I)+ALF*DX(I)
   INOUT=0
   CALL GAUSS(INOUT)
   C
   C   INOUT = 7 INDICATES PATHOLOGICAL X VALUE FOR GAUSS CALCULATION.
C
IF(INOUT.EQ.7) GO TO 305
HOLD=.FALSE.
IF(Fff.GE.FMIN) GO TO 28
FNEXT=FMIN
FMIN=Fff
ANEXT=AMIN
AMIN=ALF
GO TO 29
28 IF(Fff.GE.FNEXT) GO TO 29
FNEXT=Fff
ANEXT=ALF
27 FORMAT(' LOOKS =',13,' ALF =',F10.5, ' FFF =',F15.9, ' AMIN =',
1 F10.5,' FMIN =',F12.6,' ANEXT =',F10.5,' FNEXT =',F12.6)
29 CONTINUE
WRITE(6,27) LOOKS, ALF, FFF, AMIN, FMIN, ANEXT, FNEXT
GO TO (29,29,29,150,180,260,320) IR
C
C F1,F3,F5,F7,F9, ARE FUNC VALUES AT EVENTLY SPACED POINTS WITH
C SEPARATION DELTA. SET(I)=.TRUE INDICATES THAT F(I) HAS BEEN
C EVALUATED. DELTA MAY INCREASE OR DECREASE BY FACTORS OF 2. 0.
C F VALUES SHIFT LEFT OR RIGHT SO THAT F5 IS ALWAYS LOWEST.
C
150 DELTA=ABS(AMIN-ANEXT)
    BACK=.FALSE.
    DO 155 I=1,9
155 SET(I)=.FALSE.
    F5=FMIN
    SET5=.TRUE.
    K=3
    IF(AMIN.LT.ANEXT) K=7
F(K)=FNEXT
SET(K)=.TRUE.
160 IF(SET7) GO TO 230
   IF(SET3) GO TO 200
   IF(BACK) GO TO 250
170 ALF=AMIN+DELTA
   IR=5
   GO TO 10
180 F7=FFF
   SET7=.TRUE.
   IF(ALF.NE.AMIN) GO TO 160
C
C   SHIFT LEFT
C
   DO 190 I=1,7
      SET(I)=SET(I+2)
190  F(I)=F(I+2)
   SET8=.FALSE.
   SET9=.FALSE.
   GO TO 160
200 CONTINUE
   IF(SET1) GOTO 210
   IF(.NOT.SET1) GO TO 170
C
C   EXTRAPOLATE USING F1,F3, AND F5
C   INCREASE STEP SIZE IF F9 IS PREDICTED TO BE LOWER THAN F7.
C   DECREASE STEP SIZE IF F4 IS PREDICTED TO BE LOWER THAN F5.
C
210 BACK=4.D+00*F3.LT.(F1+3.D+00*F5)
   IF(SET9.OR.HOLD) GO TO 215
   IF(5.D+00*F3.GT.(2.D+00*F1+3.D+00*F5)) GO TO 220
215 IF(SET4) GO TO 170
    AIF=6.D+00*F3.GT.(F1+5.D+00*F5)
    IF(AIF) GO TO 170
    IF(.NOT.AIF) GO TO 305
220 DELTA=DELTA+DELTA
    F4=F3
    F3=F1
    F6=F7
    F7=F9
    SET4=SET3
    SET3=SET1
    SET0=SET7
    SET7=SET9
    SET1=.FALSE.
    SET2=.FALSE.
    SET8=.FALSE.
    SET9=.FALSE.
    GO TO 160
230 IF(SET3) GO TO 300
    IF(SET9) GO TO 240
    IF(.NOT.SET9) GO TO 250
    BACK=4.D+00*F7.GT.(F9+3.D+00*F5)
240 IF(SET1.0R.HOLD) GO TO 245
    IF(5.D+00*F7.GT.(2.D+00*F9+3.D+00*F5)) GO TO 220
245 IF(SET6) GO TO 250
    AIF=6.D+00*F7.GT.(F9+5.D+00*F5)
IF(AIF) GO TO 250
IF(.NOT.AIF) GO TO 305

250 ALF=AMIN-DELTA
IR=6
GO TO 10

260 F3=F3
   SET3=.TRUE.
   IF(ALF.NE.AMIN) GO TO 160
   DO 270 I=1,7
   SET(10-I)=SET(8-I)
270 F(10-I)=F(8-I)
   SET1=.FALSE.
   SET2=.FALSE.
   GO TO 160

C
C INTERPOLATE USING F3, F5, AND F7.
C EITHER IMMEDIATELY ATTEMPT QUADRATIC FIT OR FIRST REDUCE STEP SIZE
C IF AMIN=ZERO STEP SIZE MAY BE REDUCED BY A FACTOR OF 2, 4, 8, OR 16
C IN OTHER CASES STEP SIZE IS REDUCED BY A FACTOR OF 2.

300 DUM=F3
   IF(F7.GT.F3) DUM=F7
   SPREAD=DUM-F5
   TOL=(FNOT-FMIN)*5.D-01
   IF(TOL.LT.1.D+03*NOISE) TOL=1.D+03*NOISE
   IF(.NOT.EXACT) TOL=TOL+TOL
   DUM=F3-F5-F5+F7
   CURVE=DUM/(2.D+00*DELTA*DELTA)
   DUM=(F3-F7)/DUM
   BACK=DUM.LT.0.D+00
   IF(SPREAD.LT.TOL) GO TO 310
IF(ABS(DUM).GT.75.D-02.0R.AMIN.NE.0.D+00) GO TO 305
SET1=SET4
F1=F4
SET9=SET6
F9=F6
SET2=.FALSE.
SET3=.FALSE.
SET4=.FALSE.
SET6=.FALSE.
SET7=.FALSE.
SET8=.FALSE.
DELTA=25.D-02*DELTA
IF(ABS(DUM).GT.375.D-0.3) GO TO 160
SET1=.FALSE.
SET9=.FALSE.
DELTA=5.D-1*DELTA
IF(ABS(DUM).GT.1875.D-0.1) GO TO 160
DELTA=5.D-1*DELTA
GO TO 160
C
C CUT STEP SIZE IN HALF
C
305 DELTA=5.D-01*DELTA
   HOLD=.TRUE.
   SET1=SET3
   SET3=SET4
   SET9=SET7
   SET7=SET6
   SET2=.FALSE.
   SET4=.FALSE.
   SET6=.FALSE.
SET8=.FALSE.
F1=F3
F3=F4
F9=F7
F7=F6
GO TO 160

C
C ATTEMPT QUADRATIC FIT
C

310 ALF=AMIN+DUM*DELTA*5.D-1
   FQUAD=F5-(F3-Fi)*DUM*125.D-03
   IR=7
   GO TO 10

320 IF(.NOT.EXACT) GO TO 15
   TOL=(FNOT-FMIN)*25.D-03
   IF(TOL.LT.NOISE) TOL=NOISE
   IF(ABS(FFF-FQUAD).LT.TOL) GO TO 15
   AIF=ALF.EQ.AMIN.OR.ALF.EQ.ANEXT
   IF(AIF) GO TO 150
   IF(.NOT.AIF) GO TO 305

END

SUBROUTINE TRUDGE(K,FUNC)
IMPLICIT REAL*8(A-H,O-Z)

C PROGRAM MINIMIZES A FUNCTION OF N VARIABLES BY A MODIFIED POWELL METHOD OF SEARCH ALONG CONJUGATE DIRECTIONS. COLUMNS OF V MATRIX ARE CURRENT SEARCH DIRECTIONS. COLUMNS 1 TO K ARE (APPROXIMATELY) CONJUGATE.

C WHEN SUBROUTINE IS ENTERED WITH RESTART=.TRUE. THEN VALUES OF K AND ALL QUANTITIES IN COMMON T1 SHOULD HAVE BEEN SET PREVIOUSLY
C BY THE CALLING PROGRAM.
C WHEN TRUDGE IS CALLING WITH K NEGATIVE THEN ONLY REQUIRED VALUES
C ARE TIMLIM,TOLF,TOLR,NOISE,N,AND R.(NOISE NEEDED FOR SEARCH)
C IN THIS CASE INITIAL VALUES OF K,JSTART,RESTART,ALPH,V ARE IGNORED
C IF TRUDGE IS CALLED WITH NON-NEGATIVE K AND RESTA-T=.FALSE. THEN
C VALUES OF TIMLIM,TOLF,TOLR,NOISE,N,R,AND V ARE REQUIRED.
C IN THIS CASE K IS RESET TO ZERO AFTER FIRST PASS.
C
C EXTERNAL FUNCTION FUNC(INOUT)
C INOUT=  2 FUNCTION READS MINIMAL STARTING DATA AND EVALUATES F(R
C INOUT=  1 FUNCTION READS ALL RESTART DATA AND EVALUATES F(R)
C INOUT=  0 FUNCTION EVALUATES F(R)
C INOUT= -1 FUNCTION PUNCHES DATA FOR FUTURE CALL FUNC(1)
C INOUT= -2 FUNCTION EVALUATES F(R) AND PRINTS OUTPUT.
C
COMMON/T1/ N,NMAX,F, R(90),DR(90),CURVE,ALPHA,NOISE,EXACT,ALPH(90)
1,RNOT(90), V(90,90), CURV(90),RESTART, JSTART, FNOT, TIMLIM,
2 TOLF,TOLR
COMMON/EIGMAT/G(90,90),Q(90,90),SCRAP1(90),SCRAP2(90),SCRAP3(90)
DIMENSION P(90),U(90)
LOGICAL EXACT, RESTART
REAL*8 NOISE
EXTERNAL FUNC
NMAX=90
IF(N.GT.NMAX) STOP 'N GT 90'
FN=N
INOUT=0
IF(K.LT.0) GO TO 15
IF(.NOT.RESTART) CALL FUNC(INOUT)
DO 10 I=1,N
10 IF(ALPH(I).LE.0.D+00) ALPH(I)=1.D-01
IF(JSTART.LE.0.OR.JSTART.GT.N) JSTART=N
J=JSTART
RESTART=RESTART.AND.K.NE.N
GO TO 100

C

IF K NEGATIVE SET INITIAL V MATRIX TO IDENTITY,STANDARD VALUES.

C

15 K=N
RESTART=.FALSE.
CALL FUNC(INOUT)
DO 30 I=1,N
ALPH(I)=1.D-01
DO 20 J=1,N
20 V(I,J)=0.D+00       CURV(I)=0.D+00
30 V(I,J)=1.D+00       J=N

C

SEARCH ALONG J-TH DIRECTION FOR LOCAL MINIMUM

C

100 DO 105 I=1,N
105 DR(I)=V(I,J)
      EXACT=J.LE.K
      ALPHA=ALPH(J)
      ALFSET=ALPHA
      CALL SEARCH(LEAVE,FUNC)
      WRITE(6,120) CURVE,ALPIIA
120 FORMAT(17H NEW CURVATURE =,E13.5,10H ALPHA =,F12.7)
121 FORMAT(17H OLD CURVATURE =,E13.5,10H ALFSET=,F12.7)
122 FORMAT(20X,:10H ABNORMAL RETURN FROM SEARCH )
      ALPHA=ABS(ALPHA)
      IF(ALPHA.LT.5.D-01*ALFSET) ALFSET=5.D-01*ALFSET
      IF(ALPHA.LT.25.D-02*ALFSET) ALFSET=5.D-1*ALFSET
IF(ALPHA.GT.2.D+00*ALFSET) ALFSET=2.D+00*ALFSET
IF(ALPHA.GT.4.D+00*ALFSET) ALFSET=2.D+00*ALFSET
WRITE(6,121) CURV(J),ALFSET
CURV(J)=CURVE
ALPH(J)=ALFSET
IF(J.EQ.1) GO TO 175
J=J-1
GO TO 100
C

CALL FUNC(-1) CAUSES ALL RESTART DATA TO BE OUTPUT,
C  THIS INCLUDES ALL DATA REQUIRED FOR FUTURE CALL FUNC(1).
C
150 WRITE(6,155) K,TIMLIM,TOLF,TOLR,NOISE,J,FNOT
155 FORMAT(110,F10.0,3E10.1,110,F20.10)
       INOUT=-2
       CALL FUNC(INOUT)
       DO 160 I=1,N
160 WRITE( 6,161)I,RNOT(I),CURV(I),ALPH(I)
161 FORMAT(I5,3E20.10)
       I1=1
165 I2=I1+7
       IF(I2.GT.N) I2=N
       DO 166 L=1,N
166 WRITE(6,168)(V (L,I),I=I1,I2)
168 FORMAT(8F10.7)
       I1=I2+1
       IF(I1.LE.N) GO TO 165
       K=0
       RETURN
C
C  END OF SEQUENCE OF SEARCH ALONG ALL DIRECTIONS IN V MATRIX.
C
175 IF(RESTART) GO TO 185
   DO 180 I=1,N
180 RNOT(I)=R(I)
   RESTART=.TRUE.
   FNOT=F
   K=0
   J=N
   GO TO 180
C
C  GENERATE NEW CONJUGATE DIRECTION IF NOT CONVERGED.
C
185 DRDR=0.D+00
   DO 188 I=1,N
   DUM=R(I)-RNOT(I)
   DR(I)=DUM
188 DRDR=DUM*DUM+DRDR
   ALFSET=SQRT(DRDR)
   ALPHA=ALFSET
   IF(ALPHA.EQ.0.D+00) GO TO 192
   DO 190 I=1,N
   U(I)=DR(I)/ALFSET
190 DR(I)=U(I)
   EXACT=.TRUE.
   CALL SEARCH(LEAVE,FUNC)
   IF(LEAVE.NE.0) WRITE(6,122)
   WRITE(6,120) CURVE,ALPHA
C  ALPHA=ABS(ALPHA)
192 DELF=FNOT-F
   FNOT=F
   DRDR=0.D+00
DO 195 I=1,N
    DRDR=(R(I)-RNOT(I))**2+DRDR
195 RNOT(I)=R(I)
    DELR=SQRT(DRDR/FN)
    WRITE(6,210) F, DELF, DELR
210 FORMAT(4H F=,F20.10,10H DELTA F=,E15.5,10H DELTA R=,E15.5)
    IF(DELF.GT.TOLF.OR.DELR.GT.TOLR) GO TO 220
    WRITE(6,215)
215 FORMAT(6H /,' CONVERGED')
    GO TO 150
220 IF(K.GT.0) GO TO 230
    K=1
    K1=0
    DO 225 I=1,N
225 R(I)=DR(I)
    DR(N)=CURVE
    P(I)=ALPHA
    GO TO 375
C
C    CALCULATE K+1 Q VECTORS.Q(I) DOT V(J)=KRONIKER DELTA(I,J),I=1,K
C
230 DO 250 J=1,K
    DOT=0.D+00
    DO 240 I=1,N
240 DOT=DOT+DR(I)*V(I,J)
    P(J)=DOT
    DO 250 I=1,N
250 DR(I)=DR(I)-DOT*V(I,J)
    DOT=0.D+00
    DO 260 I=1,N
260 DOT=DR(I)*U(I)+DOT
    K1=K
K = K1 + 1
RESTART = K. NE. N
DO 270 I = 1, N
DUM = DR(I) / DOT
Q(I, K) = DUM
DO 270 J = 1, K1
270 Q(I, J) = V(I, J) - P(J) * DUM
C
C G MATRIX = SUM L = 1, K + 1 OF Q(L) * CURV(L) * TRANSPOSE Q(L)
C
DO 280 I = 1, N
DUM = CURVE * Q(I, K)
DO 280 J = 1, N
280 G(I, J) = DUM * Q(J, K)
DO 300 L = 1, K1
DO 300 I = 1, N
DUM = CURV(L) * Q(I, L)
DO 300 J = 1, N
300 G(I, J) = DUM * Q(J, L) + G(I, J)
CALL EIGN(N, DR)
C
C SET P(J) EQUAL TO CORRESPONDING ALPH VALUE.
C
DO 350 J = 1, K
JJ = N + 1 - J
P(J) = ALPH(J)
DOT = 0. D + 00
DO 310 I = 1, N
R(I) = Q(I, JJ)
310 DOT = R(I) * V(I, J) + DOT
DOT = ABS(DOT)
IF(DOT.GT.7.D-01) GO TO 350
LMAX = J
DOTMAX = DOT
DO 340 L=1,K1
IF(L.EQ.J) GO TO 340
DOT=0.D+00
DO 320 I=1,N
320 DOT=R(I)*V(I,L)+DOT
DOT=ABS(DOT)
IF(DOT.LT.7.D-01) GO TO 330
P(J)=ALPH(L)
GO TO 350
330 IF(DOT.LE.DOTMAX) GO TO 340
DOTMAX=DOT
LMAX=L
340 CONTINUE
P(J)=ALPH(LMAX)
DOT=0.D+00
DO 345 I=1,N
345 DOT=R(I)*U(I)+DOT
IF(ABS(DOT).GT.DOTMAX) P(J)=ALPHA
350 CONTINUE
C SET NEV CONJUGATE VECTORS IN V EXCEPT KTH VECTOR IS SAVED IN R.
C DO 370 J=1,K1
JJ=N+1-J
DO 360 I=1,N
360 V(I,J)=Q(I,JJ)
ALPH(J)=P(J)
370 CURV(J)=DR(JJ)
C
C ORTHOGONALIZE REMAINING SEARCH DIRECTIONS TO CONJUGATE DIRECTIONS.
C
375 IF(K.EQ.N) GO TO 450
DO 420 J=K,N
DOT=0.D+00
DO 380 I=1,N
380 DOT=V(I,J)*R(I)+DOT     DO 390 I=1,N
390 V(I,J)=V(I,J)-DOT*R(I)   IF(K.EQ.1) GO TO 420
DO 410 L=1,K1
DOT=0.D+00
DO 400 I=1,N
400 DOT=V(I,J)*V(I,L)+DOT     DO 410 I=1,N
410 V(I,J)=V(I,J)-DOT*V(I,L)  420 CONTINUE    CMAX=0.D+00
DO 425 L=K,N
425 IF(CURV(L).GT.CMAX) CMAX=CURV(L)  C    C CONSTRUCT G MATRIX FOR
REMAINING SEARCH DIRECTIONS.  C    CMAX=8.D+00*CMAX
DO 440 I=1,N
DO 440 J=1,I
DUM=CMAX*R(I)*R(J)
DO 430 L=K,N
430 DUM=CURV(L)*V(I,L)*V(J,L)+DUM     IF(K1.LE.0) GO TO 435
DO 433 L=1,K1
433 DUM=-CMAX*V(I,L)*V(J,L)+DUM     435 G(I,J)=DUM     440 G(J,I)=DUM  C    C
SET KTH CONJUGATE DIRECTIONS BACK INTO V MATRIX.  C
450 DO 460 I=1,N
460 V(I,K)=R(I)
R(I)=RNOT(I)   ALPH(K)=P(K)
CURV(K)=DR(N+1-K)
IF(K.EQ.N) GO TO 480
CALL EIGN(N,DR)
C     C  SET REMAINING SEARCH DIRECTIONS INTO V MATRIX.
C
K1=K+1
DO 470 J=K1,N
CURV(J)=DR(J)
DO 470 I=1,N
470 V(I,J)=Q(I,J) 480 J=N
GO TO 100
END
SUBROUTINE EIGN(N,EIG)
IMPLICIT REAL*8(A-H,O-Z)
REAL*8 IPOSV,IVPOS,IORD
C
C ***** VERSION 3/20/73 *****
C ***** DESCRIPTION *****
C ***** THIS IS A GIVENS-HOUSHOLDER ROUTINE *****
C ***** RECEIVES A MATRIX-A-OF WHICH ONLY LOWER *****
C ***** TRANGLE IS USED AND THIS IS DESTROYED *****
C ***** EIGENVALUES ARE RETURNED IN ALGEBRAIC *****
C ***** ASCENDING ORDER IN ARRAY-EIG- *****
C ***** THE EIGENVECTORS ARE RETURNED STORED BY *****
C ***** COLUMNS IN VEC. *****
C ***** PARAMETERS PASSED *****
C ***** RHO=TOLERANCE ON FINAL OFF-DIAG ELEMENTS *****
C ***** N IS THE SIZE OF THE MATRIX *****
C ***** OF THAT IN QCPE PROGRAM CINDO BY DOBOSH *****
C ***** THIS ROUTINE IS SLIGHTLY MODIFIED VERSION *****
C
DIMENSION W(90),EIG(90),GAMMA(90),BETA(90),P(90),Q(90),BETASQ(90)
COMMON /EIGMAT/(A(90,90),VEC(90,90),IPOSV(90),IVPOS(90),IORD(90)
EQUIVALENCE (IPOSV,GAMMA),(IVPOS,BETA),(IORD,BETASQ),
* (IVPOS,P),(IVPOS,Q) RHO=1.0D-10
RHOSQ=RHO*RHO
IF(N.EQ.0) GO TO 560
SHIFT = 0.D-00
N1=N-1
N2 = N-2
GAMMA(1) = A(1,1)
IF(N2.EQ.0) GO TO 270
IF(N2.LT.0) GO TO 280
DO 260 NR=1,N2
B = A(NR+1,NR)
S = 0.D+00
DO 130 I=NR,N2
130 S = S + A(I+2,NR)**2
C ***** PREPARE FOR POSSIBLE BYPASS OF TRANSFORMATION *****
A(NR+1,NR) = 0.D+00
IF(S.LE.0) GO TO 250
S = S + B*B
SGN = +1.D+00
IF(B.GE.0) GO TO 160
SGN = -1.D+00
160 SQRTS = SQRT(S)
D = SGN/(SQRTS + SQRTS)
TEMP = SQRT(5.D-01 + B*D)
W(NR) = TEMP
A(NR+1,NR) = TEMP
D = D/TEMP
B = -SGN*SQR
C ***** D IS FACTOR OF PROPORTIONALITY. *****
C ***** COMPUTE AND SAVE W VECTOR
DO 170 I=NR,N2
TEMP = D*A(I+2,NR)
W(I+1) = TEMP
170 A(I+2,NR) = TEMP
C ***** PREMULTIPLY VECTOR-W-BY MATRIX -A- TO OBTAIN *****
C ***** -P- VECTOR. SIMULTANEOUSLY ACCUMULATE DOT *****
C ***** PRODUCT WP,(THE SCALAR K).

\[
\text{WTAW} = 0.0 + 0.0
\]

\[
\text{DO 220 I=NR,N1}
\]

\[
\text{SUM} = 0.0 + 0.0
\]

\[
\text{DO 180 J=NR,I}
\]

180 \text{SUM}=\text{SUM}+\text{A}(I+1,J+1)*W(J)

\[
\text{II}=I+1
\]

\[
\text{IF}((N1-11),LT,0) \text{ GO TO 210}
\]

\[
\text{DO 200 J=II,N1}
\]

200 \text{SUM}=\text{SUM}+\text{A}(J+1,I+1)*W(J)

210 \text{P}(I)=\text{SUM}

220 \text{WTAW}=\text{WTAW}+\text{SUM}*W(I)

C ***** P VECTOR AND SCALAR K NOW STORED.NEXT *****

C ***** COMPUTE -Q- VECTOR *****

\[
\text{DO 230 I=NR,N1}
\]

230 \text{Q}(I)=\text{P}(I)-\text{WTAW}*W(I)

C ***** NOW FORM PAP MATRIX, REQUIRED PART *****

\[
\text{DO 240 J=NR,N1}
\]

QJ=Q(J)

WJ=W(J)

\[
\text{DO 240 I=J,N1}
\]

240 \text{A}(I+1,J+1)=\text{A}(I+1,J+1)-2.0+0.0*(W(I)*QJ+WJ*Q(I))

250 \text{BETA}(NR)=B

\text{BETASQ}(NR)=B*B

260 \text{GAMMA}(NR+1)=A(NR+1,NR+1)

270 B=\text{A}(N,N-1)

\text{BETA}(N-1)=B

\text{BETASQ}(N-1)=B*B

\text{GAMMA}(N)=A(N,N)

280 \text{BETASQ}(N)=0.0 + 0.0

C ***** ADJOIN AN IDENTITY MATRIX TO BE *****
C  ***** POSTMULTIPLIED BY ROTATIONS  *****
    DO 300 I=1,N
    DO 290 J=1,N
  290 VEC(I,J)=0.D+00
  300 VEC(I,I)=1.D+00
    M=N
    SUM=0.D+00
    NPAS=1
    GO TO 400
  310 SUM=SUM+SHIFT
    COSA=1.D+00
    G=GAMMA(1)*SHIFT
    PP=G
    PPBS=PP*PP+BETASQ(1)
    PPBR=SQRTP(PPBS)
    DO 370 J=1,M
      COSAP=COSA
      IF(PPBS.NE.0) GO TO 320
      SINA = 0.D+00
      SINA2=0.D+00
      COSA=1.D+00
      GO TO 350
  320 SINA=BETA(J)/PPBR
      SINA2=BETASQ(J)/PPBS
      COSA=PP/PPBR
C  ***** POSTMULTIPLY IDENTITY BY P-TRANSPOSE  *****
    NT=J+NPAS
    IF(NT.LE.N) GO TO 330
    NT = N
  330 DO 340 I=1,NT
      TEMP=COSA*VEC(I,J)+SINA*VEC(I,J+1)
VEC(I,J+l)=-SIN A*VEC(I,J)+COS A*VEC(I,J+l)

340 VEC(I,J)=TEMP

350 DIA=GAMMA(J+1)-SHIFT
    U=SIN A2*(G+DIA)
    GAMMA(J)=G+U
    G=DIA-U
    PP=DIA*COS A-SIN A*COS A*BETA(J)
    IF(J.NE.M) GO TO 360
    BETA(J)=SIN A*PP
    BETASQ(J)=SIN A2*PP*PP
    GO TO 380

360 PPBS=PP*PP+BETASQ(J+1)
    PPBR=SQRT(PPBS)
    BETA(J)=SIN A*PPBR

370 BETASQ(J)=SIN A2*PPBS

380 GAMMA(M+1)=G

C     ***** TEST FOR CONVERGENCE OF LAST DIAGONAL ELEMENT *****

NPAS=NPAS+1
    IF(BETASQ(M).GT.RHOSQ) GO TO 410

390 EIG(M+1)=GAMMA(M+1)+SUM

400 BETA(M)=0.D+00
    BETASQ(M)=0.D+00

    M=M-1
    IF(M.EQ.0) GO TO 430
    IF(BETASQ(M).LE.RHOSQ) GO TO 390

C     ***** TAKE ROOT OF CORNER 2 BY 2 NEAREST TO *****

C     ***** LOEWR DIAGONAL IN VALUE AS ESTIMATE OF *****

C     ***** EIGENVALUE TO USE FOR SHIFT *****

410 A2=GAMMA(M+1)       R2=5.D-01*A2
    R1=5.D-01*GAMMA(M)
    R12=R1+R2
DIF=R1-R2
TEMP=SQRT(DIF*DIF+BETASQ(M))
R1=R12+TEMP
R2=R12-TEMP
DIF=ABS(A2-R1)-ABS(A2-R2)
IF(DIF.LT.0) GO TO 420
SHIFT=R2
GO TO 310
420 SHIFT=R1
GO TO 310
430 EIG(1)=GAMMA(1)+SUM
C ***** INITIALIZE AUXILIARY TABLES REQUIRED FOR *****
C ***** REARRANGING THE VECTORS *****
DO 440 J=1,N
IPOSY(J)=J
IVPOS(J)=J
440 IORD(J) = J
C ***** USE A TRANSPOSITION SORT TO ORDER THE EIGENVALUES *****
M=N
GO TO .FL0
450 DO 460 J=1,M
IF(EIG(J).LE.EIG(J+1)) GO TO 460
TEMP=EIG(J)
EIG(J)=EIG(J+1)
EIG(J+1)=TEMP
ITEMP=IORD(J)
IORD(J)=IORD(J+1)
IORD(J+1)=ITEMP
460 CONTINUE
470 M=M-1
IF(M.NE.0) GO TO 450
IF(N1.EQ.0) GO TO 500
DO 490 L=1,N1
NV=IORD(L)
NP=IPOSV(NV)
IF(NP.EQ.L) GO TO 490
LV=IVPOS(L)
IVPOS(NP)=LV
IPOSV(LV)=NP
DO 480 I=1,N
TEMP=VEC(I,L)
VEC(I,L)=VEC(I,NP)
480 VEC(I,NP) = TEMP
490 CONTINUE
500 CONTINUE
C ***** BACK TRANSFORM THE VECTORS OF THE TRIPLE *****
C ***** DIAGONAL MATRIX
DO 550 NRR=1,N
K=N1
510 K=K-1
IF(K.LE.0) GO TO 540
SUM = 0.D+00
DO 520 I=K,N1
520 SUM=SUM+VEC(I+1,NRR)*A(I+1,K)
SUM=SUM+SUM
DO 530 I=K,N1
530 VEC(I+1,NRR)=VEC(I+1,NRR)-SUM*A(I+1,K)
540 CONTINUE
550 CONTINUE
560 CONTINUE
RETURN
END
INPUT FILE

run MANYBODY
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1836.1515
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+1.0d+00
+1.0d+00
-1.0d+00
0.0D+00
2
1,2,3
2,1,3
1,2,3
1,3,2
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1.0D+00
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OUTPUT FILE

PROGRAM NONADAIABAT FOR MOLECULAR NONADIABATIC CALCULATION
WITH EXPLICITLY CORRELATED GAUSSIAN-CLUSTER TYPE WAVEFUNCTION

*** INPUT PARAMETERS ***
NUMBER OF PARTICLES N = 3
NUMBER OF GAUSSIAN CLUSTERS USED IN EXPANSION M = 8
TOTAL NUMBER NONLINEAR PARAMETERS NLP = 48

MOLECULAR PARAMETERS

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PARAMATR k = 0.000000

PERMUTATIONS
TOTAL NUMBER OF PERMUTATIONS IPER = 2
ORBITAL EXONENTS PERMUTATIONS
1 2 3
2 1 3
CORRELATION EXONENTS PERMUTATIONS
1 2 3
1 3 2

SPIN-ADAPTATION COEFFICIENTS
1.000000
1.000000

OPTIMIZATION
TOTAL NUMBER OF PARAMETERS NOPT = 48
### PARAMETERS FOR ORBITAL EXPONENTS

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<td>0.109948E-02</td>
</tr>
<tr>
<td>16</td>
<td>0.449602E+00</td>
</tr>
<tr>
<td>17</td>
<td>0.479593E+00</td>
</tr>
<tr>
<td>18</td>
<td>0.723282E-03</td>
</tr>
<tr>
<td>19</td>
<td>0.463314E+00</td>
</tr>
<tr>
<td>20</td>
<td>0.474420E+00</td>
</tr>
<tr>
<td>21</td>
<td>0.131799E-02</td>
</tr>
<tr>
<td>22</td>
<td>0.484967E+00</td>
</tr>
<tr>
<td>23</td>
<td>0.493223E+00</td>
</tr>
<tr>
<td>24</td>
<td>0.287117E-03</td>
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### PARAMETERS FOR CORRELATION EXPONENTS

<table>
<thead>
<tr>
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<th>Value</th>
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<tbody>
<tr>
<td>1</td>
<td>0.313413E+00</td>
</tr>
<tr>
<td>2</td>
<td>-0.128255E-01</td>
</tr>
<tr>
<td>3</td>
<td>0.277373E+00</td>
</tr>
<tr>
<td>4</td>
<td>0.932051E+00</td>
</tr>
<tr>
<td>5</td>
<td>0.279734E+00</td>
</tr>
</tbody>
</table>
6  0.760317E+00
7  -1.131304E+00
8  0.528921E-01
9  0.135044E+01
10  -0.694192E-01
11  0.198463E-01
12  0.247345E+00
13  0.945101E-01
14  0.901373E-03
15  0.278774E+00
16  0.278934E+00
17  0.140664E-02
18  0.165565E+01
19  0.177182E-01
20  0.395339E-01
21  0.163547E+01
22  0.402906E-02
23  0.992747E-02
24  0.272868E+00

NORMALIZATION = 0.9999999999999973
ENERGY = -0.5711156303820003
TCM = -4.0520604717213170E-04
J[f;k] = -0.5741156303820003

********************************************************************************
EXPANSION COEFFICIENTS
********************************************************************************

C( 1) = 0.7808038999D-01
C( 2) = 0.7128937440D-01
C( 3) =-0.1356615214D-01
C( 4) =-0.1079085240D+01
C( 5) = -0.4933797503D+01
C( 6) = -0.5410428020D+00
C( 7) = 0.6959021021D+00
C( 8) = 0.6455986448D+01

*******************************
SQUARE OF INTERPARTICLE DISTANCES
*******************************
R**2(1,2) = 0.5469325853D+01
R**2(1,3) = 0.4168363608D+01
R**2(2,3) = 0.4168363608D+01

*******************************
NONLINEAR PARAMETERS
*******************************
rr( 1) = 0.3797832523D+00
rr( 2) = 0.4924046425D+00
rr( 3) = -0.330873019.10-02
rr( 4) = 0.8509846392D+00
rr( 5) = 0.3449385521D+00
rr( 6) = 0.8972519180D-01
rr( 7) = 0.5246059297D+00
rr( 8) = 0.5197150919D+00
rr( 9) = 0.1430704597D-01
rr(10) = 0.4400559070D+00
rr(11) = 0.4669636261D+00
rr(12) = -0.2940994615D-03
rr(13) = 0.4878255737D+00
rr(14) = 0.4902148987D+00
rr(15) = 0.1099483105D-02
rr(16) = 0.4496019972D+00
rr(17) = 0.4795931703D+00
rr(18) = 0.7232817748D-03
\[
\begin{align*}
rr(19) &= 0.4633142957D+00 \\
rr(20) &= 0.4744199973D+00 \\
rr(21) &= 0.1317987569D-02 \\
rr(22) &= 0.4849667638D+00 \\
rr(23) &= 0.4838360412D+00 \\
rr(24) &= 0.8097372174D-03 \\
rr(25) &= 0.2868015006D+00 \\
rr(26) &= 0.1228980774D+00 \\
rr(27) &= 0.2707673663D+00 \\
rr(28) &= 0.2783102061D+01 \\
rr(29) &= 0.2839240450D+00 \\
rr(30) &= -0.3313561498D-01 \\
rr(31) &= -0.1683679781D+00 \\
rr(32) &= -0.778696874D-02 \\
rr(33) &= 0.1555721032D+01 \\
rr(34) &= -0.7127968828D-01 \\
rr(35) &= 0.173730459D-01 \\
rr(36) &= 0.2536515200D+00 \\
rr(37) &= 0.924013661D-01 \\
rr(38) &= 0.1041601573D+02 \\
rr(39) &= 0.2790242433D+00 \\
rr(40) &= 0.283281841D+00 \\
rr(41) &= 0.1086201294D-01 \\
rr(42) &= 0.1655651782D+01 \\
rr(43) &= 0.3308378666D-01 \\
rr(44) &= 0.3469241766D-01 \\
rr(45) &= 0.1660915087D+01 \\
rr(46) &= 0.2471112265D-02 \\
rr(47) &= 0.1003779278D-01 \\
rr(48) &= 0.2716099771D+00 
\end{align*}
\]
REFERENCES

[95] a) GAUSSIAN 90, Revision I, M. J. Frish, M. Head-Gordon, G. W. Trues, J. B. Foresman, H. B. Schlegel, C. Gonzales, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, Gaussian, Inc., Pittsburg PA, 1990;
c) GAMMIES, program QG01 assembled by M. Dupuis, D. Spangler, and J. J. Wendoloski, National Resource for Computations in Chemistry, University of California, Berkeley, CA, 1980.