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Algorithms for calculating mass-velocity and Darwin relativistic corrections with *n*-electron explicitly correlated Gaussians with shifted centers

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Algorithms for calculating the leading mass-velocity (MV) and Darwin (D) relativistic corrections are derived for electronic wave functions expanded in terms of *n*-electron explicitly correlated Gaussian functions with shifted centers and without pre-exponential angular factors. The algorithms are implemented and tested in calculations of MV and D corrections for several points on the ground-state potential energy curves of the H_2 and LiH molecules. The algorithms are general and can be applied in calculations of systems with an arbitrary number of electrons. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4947553]

I. INTRODUCTION

In high-accuracy quantum-mechanical molecular calculations, the quantum electrodynamics (QED) provides a general theoretical framework for including relativistic and QED corrections. The zeroth-order level in such an approach is the nonrelativistic Schrödinger equation and the perturbation Hamiltonian representing the relativistic effects is derived based on the so–called non-relativistic QED theory (NRQED).[1–4] In this theory, the relativistic corrections appear as quantities proportional to powers of the fine structure parameter α (where $\alpha = \frac{1}{c}$) and are determined using the perturbation theory. The development presented in this work involves determining the expectation value of the electronic relativistic Breit-Pauli Hamiltonian[5] representing the mass-velocity (MV) and one- and two-electron Darwin (D) relativistic corrections using the Cartesian representation of the MV and D relativistic operators. The clumped-nucleus wave functions used in the approach are expanded in terms of all-electron explicitly correlated Gaussian functions (ECGs) with shifted centers. The derived algorithms are general and can be used in calculations of systems with an arbitrary number of electrons.

Algorithms for calculating the leading electronic relativistic corrections for two-electron clumped-nucleus wave functions expanded in terms of ECGs were derived and implemented before by Cencek and Kutzelnigg.[6] They showed that careful optimization of the non-linear parameters of the ECGs not only yields accurate nonrelativistic energies but also very well converged leading relativistic corrections, even in the traditional approach employing the Pauli Hamiltonian. Recently we have used ECGs in very accurate calculations of some two-, three-, and four-electron systems, H_3^+,[7–10] LiH^+,[11] LiH,[12] He_2^+,[13] and $(H_2)_2$.[14] The calculations produced the most

accurate nonrelativistic ground-state potential-energy surfaces (PESs) for these systems ever calculated. PESes for some other four-, five-, and six-electron systems, HeH^-, BeH, Li_2, are in the process of being generated. In order to further improve the quality of these surfaces the leading relativistic corrections need to be calculated for each PES point. The present work addresses this need.

In the first part of this article we present the derivation of the matrix elements involved in the expressions for the MV and D relativistic corrections. Next we discuss the computational implementation of the derived formulas and the resulting computer code. The code is subsequently used to run some test calculations. They concern several points of the ground-state PESes of the H_2 and LiH molecules. The results are compared with literature results.

II. BASIS FUNCTIONS

The present work concerns molecular systems with only σ electrons such as H_2, H_3, and Li_2. The ground-state wave functions of these systems can be very accurately represented using expansions in terms of the following explicitly correlated Gaussian functions with shifted centers,

$$\phi_k^\sigma(\mathbf{r}) = \exp\left[-(\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k(\mathbf{r} - \mathbf{s}_k)\right] \equiv \phi_k(\mathbf{r}), \qquad (1)$$

where $\mathbf{r}$ is a $3n$-dimensional vector of the spatial coordinates of the n electrons forming the system, $\mathbf{s}_k$ is a $3n$-dimensional vector of the Cartesian coordinates of the Gaussian shifts, T denotes vector transposition, and $\underline{\mathbf{A}}_k$ is a $3n \times 3n$ dimensional symmetric matrix of the Gaussian exponential parameters defined as

$$\underline{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3, \qquad (2)$$

with $\mathbf{I}_3$ being a 3×3 identity matrix, $\otimes$ denoting the Kronecker product, and $\mathbf{A}_k$ being a $n \times n$ symmetric matrix. For linear molecules, Gaussian shifts $\mathbf{s}_k$ are confined to the molecular axis and for a planar molecule, like H_3^+, they are confined to

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the molecular plane. For Gaussian (1) to be square integrable, as a basis function used for expanding the wave function of a bound electronic state should be, $\mathbf{A}_k$ has to be positive definite. This automatically happens if $\mathbf{A}_k$ is represented in the Cholesky-factored form as $\mathbf{L}_k\mathbf{L}_k^T$ with $\mathbf{L}_k$ being a lower triangular matrix whose elements are real numbers ranging from $-\infty$ to $+\infty$. This feature is particularly important in the variational optimization of the Gaussians, as it allows to perform this optimization in terms of the $\mathbf{L}_k$ matrix elements without any restrictions, i.e., in the $(-\infty, +\infty)$ range. In the optimization approach we developed, we employ the analytically calculated energy gradient determined in terms of the $\mathbf{L}_k$ matrix elements.[15] The use of the gradient considerably accelerates the optimization process and allows for achieving high accuracy of the results.

III. MATRIX ELEMENTS FOR THE MV AND D RELATIVISTIC CORRECTIONS

The operators representing the MV and D relativistic corrections can be separated into one-electron and two-electron contributions. The one-electron parts are

$$\hat{H}_{\mathrm{MV}} = -\alpha^2 \frac{1}{8} \sum_{i=1}^{n} \mathbf{p}_i^4, \tag{3}$$

$$\hat{H}_{\mathrm{d1}} = -\alpha^2 \frac{1}{8} \sum_{a=1}^{N} Q_a \sum_{i=1}^{n} \nabla_{\mathbf{r}_i}^2 \frac{1}{r_{ia}}, \tag{4}$$

where $\mathbf{p}_i$ momentum operator for the ith electron, $\mathbf{r}_{ia}$ is the distance between the ith electron and the a-th nucleus, and N is the number of the nuclei. The operator representing the two-electron D correction is

$$\hat{H}_{\mathrm{d2}} = \alpha^2 \frac{1}{4} \sum_{i>j}^{n} \nabla_{\mathbf{r}_i}^2 \frac{1}{r_{ij}}. \tag{5}$$

The total operator representing the MV and D relativistic corrections used in the present work is

$$\alpha^2 \mathrm{E}_{\mathrm{rel}} = \langle \hat{H}_{\mathrm{MV}} + \hat{H}_{\mathrm{d1}} + \hat{H}_{\mathrm{d2}} \rangle. \tag{6}$$

The derivation of the individual contributions to $\mathrm{E}_{\mathrm{rel}}$ are presented next.

A. Mass-velocity correction

The matrix element for ECGs ϕ_k and ϕ_l calculated with the operator representing the MV correction

$$\hat{H}_{\mathrm{MV}} = -\alpha^2 \frac{1}{8} \sum_{i=1}^{n} \nabla_{\mathbf{r}_i}^4 \tag{7}$$

has the following form:

$$\langle \phi_k | \hat{H}_{\mathrm{MV}} | \phi_l \rangle = -\frac{\alpha^2}{8} \sum_{i=1}^{n} \langle \nabla_{\mathbf{r}_i}^2 \phi_k | \nabla_{\mathbf{r}_i}^2 \phi_l \rangle$$
$$= -\frac{\alpha^2}{8} \sum_{i=1}^{n} \langle \left(\nabla_{\mathbf{r}}^T \underline{\mathbf{J}}_{ii} \nabla_{\mathbf{r}} \right) \phi_k | \left(\nabla_{\mathbf{r}}^T \underline{\mathbf{J}}_{ii} \nabla_{\mathbf{r}} \right) \phi_l \rangle, \tag{8}$$

where

$$\langle \left(\nabla_{\mathbf{r}}^T \underline{\mathbf{J}}_{ii} \nabla_{\mathbf{r}} \right) \phi_k | \left(\nabla_{\mathbf{r}}^T \underline{\mathbf{J}}_{ii} \nabla_{\mathbf{r}} \right) \phi_l \rangle$$
$$= \langle \phi_k | \left[-2 \mathrm{Tr}[\underline{\mathbf{A}}_k \underline{\mathbf{J}}_{ii}] + 4 (\mathbf{r} - \mathbf{s}_k)^T \underline{\mathbf{A}}_k \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}_k (\mathbf{r} - \mathbf{s}_k) \right]$$
$$\left[-2 \mathrm{Tr}[\underline{\mathbf{A}}_l \underline{\mathbf{J}}_{ii}] + 4 (\mathbf{r} - \mathbf{s}_l)^T \underline{\mathbf{A}}_l \underline{\mathbf{J}}_{ii} \underline{\mathbf{A}}_l (\mathbf{r} - \mathbf{s}_l) \right] | \phi_l \rangle. \tag{9}$$

Matrix $\mathbf{J}_{ij}$ used in the above equations is

$$\mathbf{J}_{ij} = \begin{cases} \mathbf{E}_{ii} & i = j \\ \mathbf{E}_{ii} + \mathbf{E}_{jj} - \mathbf{E}_{ij} - \mathbf{E}_{ji} & i \neq j, \end{cases}$$

where $\mathbf{E}_{ij}$ is the $n \times n$ matrix with 1 in the ijth position and 0's elsewhere. Formally this can be written as $(\mathbf{E}_{ij})_\beta^\alpha = \delta_i^\alpha \delta_{j\beta}$. It is easy to see that

$$\begin{cases} \mathbf{E}_{ij} \cdot \mathbf{E}_{ij} &= 0, \\ \mathbf{E}_{ij} \cdot \mathbf{E}_{ji} &= \mathbf{E}_{ii}, \\ \mathbf{E}_{ij} \cdot \mathbf{E}_{jj} &= \mathbf{E}_{ij}, \\ \mathbf{E}_{ji} \cdot \mathbf{E}_{ii} &= \mathbf{E}_{ji}. \end{cases} \tag{10}$$

The following integrals need to be derived to evaluate expression (9):

$$\langle \phi_k | (\mathbf{r}^T \underline{\mathbf{B}} \mathbf{r}) | \phi_l \rangle, \quad \langle \phi_k | (\mathbf{r}^T \underline{\mathbf{B}} \mathbf{r}) (\mathbf{r}^T \underline{\mathbf{C}} \mathbf{r}) | \phi_l \rangle,$$
$$\langle \phi_k | (\mathbf{r}^T \underline{\mathbf{B}} \mathbf{s}_n) | \phi_l \rangle, \quad \langle \phi_k | (\mathbf{r}^T \underline{\mathbf{B}} \mathbf{r}) (\mathbf{r}^T \underline{\mathbf{C}} \mathbf{s}_n) | \phi_l \rangle,$$
$$\langle \phi_k | (\mathbf{r}^T \underline{\mathbf{B}} \mathbf{s}_n) (\mathbf{r}^T \underline{\mathbf{C}} \mathbf{s}_m) | \phi_l \rangle.$$

The reader can find the derivation of the above integrals in the supplementary material.[16]

B. Darwin correction

As mentioned, the D correction consists of one- and two-electron parts. They can be calculated using two different approaches. The first approached termed "Method I" involves direct use of operators (4) and (5). In the second approach termed "Method II," the Darwin one- and two-electron operators are obtained by using the Poisson equation[5] applied to transform Darwin operators (4) and (5) to the following operators involving Dirac delta functions:

$$\hat{H}_{\mathrm{d}}^{II} = \hat{H}_{\mathrm{d1}}^{II} + \hat{H}_{\mathrm{d2}}^{II}, \tag{11}$$

where

$$\hat{H}_{\mathrm{d1}}^{II} = \alpha^2 \frac{1}{2} \pi \sum_{a=1}^{N} Q_a \sum_{i=1}^{n} \delta^3(\mathbf{r}_{ia}) \tag{12}$$

and

$$\hat{H}_{\mathrm{d2}}^{II} = -\alpha^2 \pi \sum_{i>j}^{n} \delta^3(\mathbf{r}_{ij}). \tag{13}$$

We first consider the matrix element of operator $\hat{H}_{\mathrm{d}}^{I} = \hat{H}_{\mathrm{d1}} + \hat{H}_{\mathrm{d2}}$ (see Eqs. (4) and (5)) of Method I,

$$\langle\phi_k|\hat{H}_{\mathrm{d}}^I|\phi_l\rangle = -\alpha^2\frac{1}{8}\sum_{a=1}^{N}Q_a\sum_{i=1}^{n}\left\{\langle\nabla_{\mathbf{r}_i}^2\phi_k|\frac{1}{r_{ia}}|\phi_l\rangle + \langle\phi_k|\frac{1}{r_{ia}}|\nabla_{\mathbf{r}_i}^2\phi_l\rangle + 2\,\langle\nabla_{\mathbf{r}_i}\phi_k|\frac{1}{r_{ia}}|\nabla_{\mathbf{r}_i}\phi_l\rangle\right\} \tag{14}$$

$$+\alpha^2\frac{1}{4}\sum_{i>j}^{n}\left\{\langle\nabla_{\mathbf{r}_i}^2\phi_k|\frac{1}{r_{ij}}|\phi_l\rangle + \langle\phi_k|\frac{1}{r_{ij}}|\nabla_{\mathbf{r}_i}^2\phi_l\rangle + 2\,\langle\nabla_{\mathbf{r}_i}\phi_k|\frac{1}{r_{ij}}|\nabla_{\mathbf{r}_i}\phi_l\rangle\right\} \tag{15}$$

$$=-\alpha^2\frac{1}{8}\sum_{a=1}^{N}Q_a\sum_{i=1}^{n}\left\{\langle\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_k|\frac{1}{r_{ia}}|\phi_l\rangle + \langle\phi_k|\frac{1}{r_{ia}}|\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_l\rangle + 2\,\langle\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_k|\frac{1}{r_{ia}}|\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_l\rangle\right\}$$

$$+\alpha^2\frac{1}{4}\sum_{i>j}^{n}\left\{\langle\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_k|\frac{1}{r_{ij}}|\phi_l\rangle + \langle\phi_k|\frac{1}{r_{ij}}|\nabla_{\mathbf{r}}^T\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_l\rangle + 2\,\langle\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_k|\frac{1}{r_{ij}}|\underline{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\,\phi_l\rangle\right\}. \tag{16}$$

Thus, to calculate the matrix element the following integrals need to be evaluated: $\langle\phi_k|(\mathbf{r}^T\underline{\mathbf{B}}\,\mathbf{r})\,\frac{1}{r_g}\,|\phi_l\rangle$ and $\langle\phi_k|(\underline{\mathbf{B}}\,\mathbf{s}_n)^T\mathbf{r}\,\frac{1}{r_g}\,|\phi_l\rangle$, where g stands for either ij or ia. The derivation of the integrals is shown in supplementary material.[16]

In Method II, the evaluation of the corresponding matrix element involves the following representation of the 3-dimensional Dirac delta function:[17]

$$\delta^3((\mathbf{b}\otimes\mathbf{I}_3)^T\mathbf{r}-\boldsymbol{\xi})$$
$$= \lim_{\beta\to\infty}\left(\frac{\beta}{\pi}\right)^{3/2}\exp\left[-\beta((\mathbf{b}\otimes\mathbf{I}_3)^T\mathbf{r}-\boldsymbol{\xi})^2\right], \quad (17)$$

where $\mathbf{b}$ is a real n-component vector, the result $(\mathbf{b}\otimes\mathbf{I}_3)$ is a $n\times3$ rectangular matrix and $\boldsymbol{\xi}$ is some real 3-dimensional parameter. The matrix element of delta function (the derivation of the matrix element is shown in supplementary material[16])

we find as

$$\langle\phi_k|\delta^3((\mathbf{b}\otimes\mathbf{I}_3)^T\mathbf{r}-\boldsymbol{\xi})|\phi_l\rangle$$
$$= \langle\phi_k|\phi_l\rangle\exp\left[-\mathbf{s}^T\underline{\mathbf{A}}_{kl}\mathbf{s}\right]\,\pi^{-3/2}\,\Lambda^{-3/2}$$
$$\exp\left[-\frac{1}{\Lambda}\boldsymbol{\xi}^T\boldsymbol{\xi}\,+\,\frac{1}{\Lambda}\,\mathbf{w}^T A_{kl}^{-1}\mathbf{b}\boldsymbol{\xi}\right], \tag{18}$$

where $\underline{\mathbf{A}}_{kl} = \underline{\mathbf{A}}_k + \underline{\mathbf{A}}_l$, $\mathbf{s}$ and $\mathbf{w}$ are $3n$-component vectors defined as follows: $\mathbf{s} = \underline{\mathbf{A}}_{kl}^{-1}(\underline{\mathbf{A}}_k\mathbf{s}_k + \underline{\mathbf{A}}_l\mathbf{s}_l)$, $\mathbf{w} = 2(\underline{\mathbf{A}}_k\mathbf{s}_k + \underline{\mathbf{A}}_l\mathbf{s}_l)$, while $\Lambda \equiv \mathbf{b}^T A_{kl}^{-1}\mathbf{b}$. The above formula represents a general case of the expectation value of $\delta^3((\mathbf{b}\otimes\mathbf{I}_3)^T\mathbf{r}-\boldsymbol{\xi})$ and, with an appropriate choice of vector $(\mathbf{b}\otimes\mathbf{I}_3)$, it can be used to calculate matrix elements of operators representing $\delta^3(\mathbf{r}_{ij})$ in the Darwin term $\hat{H}_{\mathrm{d}2}^{II}$ (13) and $\delta^3(\mathbf{r}_{ia})$ in the Darwin term $\hat{H}_{\mathrm{d}1}^{II}$ (12). The matrix elements $\langle\delta^3(\mathbf{r}_{ij})\rangle$ and $\langle\delta^3(\mathbf{r}_{ia})\rangle$ are obtained by setting $\mathbf{bb}^T\otimes\mathbf{I}_3 = \underline{\mathbf{J}}_{ij}$ and $\mathbf{bb}^T\otimes\mathbf{I}_3 = \underline{\mathbf{J}}_{ii}$, respectively. In the first case the matrix element has the following form:

$$\langle\phi_k|\delta^3(\mathbf{r}_{ij})|\phi_l\rangle = \langle\phi_k|\phi_l\rangle\,\exp\left[-\mathbf{s}^T\underline{\mathbf{A}}_{kl}\mathbf{s}\right]\,\pi^{-3/2}\,\mathrm{Tr}\,[A_{kl}^{-1}\mathbf{J}_{ij}]^{-3/2}$$
$$\times\exp\left[\frac{1}{\mathrm{Tr}\,[A_{kl}^{-1}\mathbf{J}_{ij}]}\frac{1}{4}\,\mathbf{e}^T\left(\mathrm{Tr}\,[A_{kl}^{-1}\mathbf{J}_{ij}]A_{kl}^{-1} - A_{kl}^{-1}\mathbf{J}_{ij}A_{kl}^{-1}\right)\mathbf{e}\right], \tag{19}$$

where $\mathbf{e} = \underline{\mathbf{A}}_k\mathbf{s}_k + \underline{\mathbf{A}}_l\mathbf{s}_l$, and in the second case the matrix element is

$$\langle\phi_k|\delta^3(\mathbf{r}_{ia})|\phi_l\rangle = \langle\phi_k|\phi_l\rangle\,\exp\left[-(\mathbf{s}-\mathbf{a})^T\underline{\mathbf{A}}_{kl}(\mathbf{s}-\mathbf{a})\right]\,\pi^{-3/2}\,\mathrm{Tr}\,[A_{kl}^{-1}\mathbf{J}_{ii}]^{-3/2}$$
$$\times\exp\left[\frac{1}{\mathrm{Tr}\,[A_{kl}^{-1}\mathbf{J}_{ii}]}\frac{1}{4}\,\mathbf{w}^T\left(\mathrm{Tr}\,[A_{kl}^{-1}\mathbf{J}_{ii}]A_{kl}^{-1} - A_{kl}^{-1}\mathbf{J}_{ii}A_{kl}^{-1}\right)\mathbf{w}\right], \tag{20}$$

where $\mathbf{w} = 2\underline{\mathbf{A}}_{kl}(\mathbf{s}-\mathbf{a})$.

IV. NUMERICAL TESTS

The formulas for the MV and D corrections derived above have been implemented on a parallel computer platform using the MPI protocol. The computer code is written in Fortran90. The code has been tested in the calculations involving the H_2 and LiH molecules. For the former system, the results are compared with the calculations of Wolniewicz[18] and

for the latter system with the calculations performed by Holka et al.[19] The present calculations of the MV and D corrections of the two systems have been performed for same selected internuclear distances sampling the full range of the corresponding potential energy curves.

The results of the H_2 calculations are shown in Table I. In the case of our calculations 1000 ECGs have been employed and for each PES point the non-linear parameters of the Gaussians, i.e., the L_k matrix elements and the elements of the $\mathbf{s}_k$ shift vector, have been extensively variationally

TABLE I. $\langle \hat{H}_{MV} \rangle$, and one- and two-electron Darwin, $\langle \hat{H}_{d1} + \hat{H}_{d2} \rangle$, relativistic corrections for the H_2 molecule at different internuclear distances, R. The corrections are reported in a.u. after multiplication by α^2. The total energy with the relativistic corrections is obtained as: $E_{rel} = E_{nr} + \langle \hat{H}_{MV} + \hat{H}_{d1} + \hat{H}_{d2} \rangle$ where E_{nr} is the nonrelativistic energy. The present results are compared with the results of Wolniewicz.[18]

R	E_{nr}	E_{nr}[18]	$\langle \hat{H}_{MV} \rangle$	$\langle \hat{H}_{MV} \rangle$[18]	$\langle \hat{H}_{d1} + \hat{H}_{d2} \rangle$	$\langle \hat{H}_{d1} + \hat{H}_{d2} \rangle$[18]	E_{rel}	E_{rel}[18]
0.40	−0.120 230 225	−0.120 230 242	−0.000 298 446	−0.000 299 072	0.000 239 460	0.000 240 095	−0.120 230 229	−0.120 230 245
0.60	−0.769 635 412	−0.769 635 353	−0.000 209 270	−0.000 209 396	0.000 170 029	0.000 170 141	−0.769 635 414	−0.769 635 355
0.80	−1.020 056 651	−1.020 056 603	−0.000 156 684	−0.000 156 779	0.000 128 835	0.000 128 909	−1.020 056 653	−1.020 056 604
0.90	−1.083 643 227	−1.083 643 180	−0.000 138 500	−0.000 138 586	0.000 114 487	0.000 114 552	−1.083 643 228	−1.083 643 181
1.00	−1.124 539 707	−1.124 539 664	−0.000 123 954	−0.000 124 030	0.000 102 944	0.000 103 002	−1.124 539 708	−1.124 539 665
1.35	−1.173 963 711	−1.173 963 683	−0.000 091 204	−0.000 091 260	0.000 076 610	0.000 076 654	−1.173 963 712	−1.173 963 684
1.40	−1.174 475 696	−1.174 475 671	−0.000 088 070	−0.000 088 123	0.000 074 051	0.000 074 093	−1.174 475 697	−1.174 475 672
1.70	−1.162 458 725	−1.162 458 688	−0.000 074 163	−0.000 074 194	0.000 062 547	0.000 062 569	−1.162 458 726	−1.162 458 689
2.00	−1.138 132 884	−1.138 132 919	−0.000 065 954	−0.000 065 985	0.000 055 507	0.000 055 575	−1.138 132 884	−1.138 132 920
2.60	−1.085 791 227	−1.085 791 190	−0.000 058 936	−0.000 058 988	0.000 049 088	0.000 049 135	−1.085 791 227	−1.085 791 191
3.40	−1.036 075 383	−1.036 075 361	−0.000 059 325	−0.000 059 363	0.000 048 435	0.000 048 477	−1.036 075 384	−1.036 075 362
4.20	−1.012 359 954	−1.012 359 938	−0.000 062 784	−0.000 062 824	0.000 050 594	0.000 050 638	−1.012 359 955	−1.012 359 939
6.00	−1.000 835 702	−1.000 835 702	−0.000 066 067	−0.000 066 187	0.000 052 856	0.000 052 974	−1.000 835 702	−1.000 835 703
8.00	−1.000 055 599	−1.000 055 603	−0.000 066 483	−0.000 066 537	0.000 053 178	0.000 053 230	−1.000 055 599	−1.000 055 604
10.00	−1.000 008 718	−1.000 008 754	−0.000 066 508	−0.000 066 560	0.000 053 196	0.000 053 248	−1.000 008 718	−1.000 008 755

optimized using the procedure employing the analytical gradient determined with respect to these parameters. 15 PES points have been considered in the calculations ranging from 0.4 a.u. to 10.0 a.u. After the optimization finished, the basis set obtained for each PEC point is checked for linear dependencies among the basis functions and if any are found the functions causing them are removed from the set. Due to this removal the average size of the basis set was reduced from 1000 ECGs to about 950 ECGs.

The nonrelativistic variational energies obtained in the calculations and the corresponding energies of Wolniewicz[18] are shown in the second and third columns in Table I. As one can see, the energies are very similar and, except for the most peripheral points our energies are slightly lower than those of Wolniewicz. In the fourth and fifth columns we compare the values of the MV corrections. As one can notice our results reproduce the results of Wolniewicz with the accuracy of three significant digits or better. Similar accuracy is also obtained for the D correction. This can be seen by comparing the results shown in the sixth and seventh columns in Table I. Finally, in columns eight and nine, the total energies obtained in the present calculations that include the MV and D relativistic corrections are compared with the corresponding energies of Wolniewicz.[18] As one can see the values are very similar

and the difference are primarily due to the differences in the non-relativistic energies.

In the calculations of the D corrections shown in Table I, we have used method I. Method II that employs Dirac delta functions is also implemented in our code. This allows for an additional verification of the results. For example, at the H_2 equilibrium distance (R = 1.4 a.u.), the results for the nucleus-electron and electron-electron D corrections (before multiplication by α^2) obtained with method I are equal to 1.443 496 555 989 50 and −0.052 616 295 209 14 a.u., respectively, while the corresponding values obtained with method II are 1.443 496 555 990 16 and −0.052 616 295 248 49 a.u., respectively. The results being virtually identical for the two methods justify the use of only one method, i.e., method I, in the calculations.

The next test calculations concern the LiH molecule. These are the first calculations of the MV and D relativistic corrections ever done for a system with more than two electrons employing wave functions expended in terms of all-electron ECGs. The literature data which can be used for comparison are much more limited than in the case of the H_2 molecule. The most recent calculations of the relativistic corrections for the LiH molecule are those of Holka *et al.*[19] However, their calculations were performed using

TABLE II. $\langle \hat{H}_{MV} \rangle$, and one- and two-electron Darwin, $\langle \hat{H}_{d1} + \hat{H}_{d2} \rangle$, relativistic corrections for the LiH molecule at different internuclear distances, R. The corrections are reported in a.u. after multiplication by α^2. The total energy with the relativistic corrections is obtained as: $E_{rel} = E_{nr} + \langle \hat{H}_{MV} + \hat{H}_{d1} + \hat{H}_{d2} \rangle$ where E_{nr} is the nonrelativistic energy. The present results are compared with the results of Holka *et al.*[19]

R	E_{nr}	$\langle \hat{H}_{MV} \rangle$	$\langle \hat{H}_{d1} \rangle$	$\langle \hat{H}_{MV} + \hat{H}_{d1} \rangle$	$\langle \hat{H}_{MV} + \hat{H}_{d1} \rangle$[19]	$\langle \hat{H}_{d2} \rangle$	E_{rel}
2.0	−8.000 761 17	−0.004 270 93	0.003 536 84	−0.000 734 10	−0.000 729 41	−0.000 094 83	−8.001 590 09
2.5	−8.058 262 45	−0.004 232 22	0.003 511 27	−0.000 720 95	−0.000 716 32	−0.000 093 18	−8.059 076 58
3.0	−8.070 540 63	−0.004 209 96	0.003 495 93	−0.000 714 03	−0.000 709 37	−0.000 092 18	−8.071 346 84
3.5	−8.064 723 19	−0.004 197 79	0.003 486 85	−0.000 710 94	−0.000 705 67	−0.000 091 57	−8.065 525 70
4.0	−8.052 249 40	−0.004 190 23	0.003 481 55	−0.000 708 68	−0.000 703 77	−0.000 091 21	−8.053 049 29
5.0	−8.024 406 73	−0.004 184 60	0.003 477 44	−0.000 707 16	−0.000 702 88	−0.000 090 89	−8.025 204 78
6.0	−8.001 976 27	−0.004 189 51	0.003 478 64	−0.000 710 86	−0.000 704 49	−0.000 090 90	−8.002 778 04
10.0	−7.978 505 11	−0.004 196 09	0.003 481 17	−0.000 714 93	−0.000 711 42	−0.000 091 37	−7.979 311 40

multi-reference configuration-interaction (MRCI) wave functions expanded in terms of Slater determinants and their relativistic correction, in addition to the MV term, only included the one-electron part of the D correction. Thus the comparison of the present results with their results only involves the sum of the MV and one-electron D corrections. That comparison is presented in Table II. Our results are obtained with the wave functions expanded in terms of 2400 ECGs generated in our previous work.[12] By comparing the fifth column in the table that contains the present results with the sixth column that contains the results of Holka *et al.*,[19] one can see quite good agreement. On average, the results differ only in the third significant digit. In the table, we also show the two-electron part of the D corrections obtained in our calculations which, as expected, is much smaller than the one-electron part. In the last column we show the sum of the non-relativistic energy and the MV and D relativistic corrections.

V. SUMMARY

Algorithms for calculating the leading MV and D relativistic corrections have been derived for the wave function expanded in terms of all-electron explicitly correlated Gaussian functions with shifted centers with no restrictions on the number of electrons. The algorithms have been implemented and tested in the calculations concerning the H_2 and LiH molecules for which previously obtained high-accuracy results exist in the literature. Good agreement of the present results and the literature results is demonstrated. This provides an evidence that the implementation is correct.

The implementation paves the way for performing high-accuracy calculations of potential energy curves and surfaces of small molecular systems with more than two electrons. The previous implementation of the analytical gradient of the variational energy with respect to the non-linear parameters of the ECGs has enabled to generate very accurate electronic wave functions expanded in terms of all-electron ECGs.[15] The present work by adding the capability to calculate relativistic corrections lifts the accuracy level of the approach even higher. The next step of the development will involve implementation of the algorithms to calculate orbit-orbit, spin-orbit, and spin-spin relativistic corrections. After that capability for calculating the non-adiabatic correction will be developed (an algorithm for calculating the adiabatic correction is already developed[15]). This will be followed by the development of algorithms for calculating the leading quantum electrodynamics (QED) corrections. These future developments will eventually enable very accurate calculations of small molecular systems with more than two electrons and with two and more nuclei.

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