PHYSICAL REVIEW A **95**, 062509 (2017)

Relativistic corrections for non-Born-Oppenheimer molecular wave functions expanded in terms of complex explicitly correlated Gaussian functions

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(Received 5 April 2017; published 26 June 2017)

In our previous work S. Bubin *et al.*, Chem. Phys. Lett. **647**, 122 (2016), it was established that complex explicitly correlated one-center all-particle Gaussian functions (CECGs) provide effective basis functions for very accurate nonrelativistic molecular non-Born-Oppenheimer calculations. In this work, we advance the molecular CECGs approach further by deriving and implementing algorithms for calculating the leading relativistic corrections within this approach. The algorithms are tested in the calculations of the corrections for all 23 bound pure vibrational states of the HD^+ ion.

DOI: 10.1103/PhysRevA.95.062509

I. INTRODUCTION

Accurate quantum mechanical calculations of bound states of molecular systems without assuming the Born-Oppenheimer (BO) approximation provide a unique way of describing these systems without any approximations concerning the separability of the motions of the nuclei and electrons. Besides the conceptual aspect of non-BO calculations, which provides an interesting view on molecular properties, these types of calculations are also capable of generating very accurate results concerning the molecular spectra. Examples of such calculations can be found in the works of Bhatia [1], Bhatia and Drachman [2,3], and Cassar and Drake [4], where Hylleraas functions were used to determine energies and other properties (polarizabilities, Stark effect, relativistic corrections, etc.) of the hydrogen molecular ion and its isotopologues.

There are significant differences between BO and non-BO calculations for a molecular system. The former involve separate calculations of the electronic wave function and the corresponding energy performed at some selected configurations of the nuclei placed in different fixed positions in space. These calculations provide the so-called potential energy surface (PES), which is used in the subsequent calculation of bound states corresponding to the rovibrational motion of the molecule. In non-BO calculations, the nuclei and the electrons forming the molecule are treated on equal footing. The calculations provide total energies and the corresponding total wave functions, which explicitly depend on the coordinates of both the nuclei and the electrons. As the electrons, particularly the core electrons, follow the nuclei in their motion in space, they have to be described using basis functions which explicitly depend on the electron-nucleus distances. The use of an orbital expansion approach in representing this motion, as well as the relative motion of the nuclei, is usually very ineffective. In our works [5,6] on the development of non-BO molecular methods, the major issue has been the selection of an appropriate basis set which is capable of describing the highly correlated motion of the electron and the nuclei in ground and excited bound states. A number of different basis sets have been implemented. All of them are different forms of explicitly correlated Gaussian (ECG) functions.

The starting point of an approach for calculating molecular bound states without assuming the BO approximation is the nonrelativistic Hamiltonian dependent on laboratory-frame coordinates of all particles forming the system. In our approach, it is a laboratory Cartesian coordinate system. As the Hamiltonian includes the internal relative motion of the particles around the center of mass of the system, as well as the motion of the center of mass in space, the two motions have to be separated so the calculation only focuses on the “internal” bound states of the system. These bound states are eigenstates of the Hamiltonian (called the internal Hamiltonian) which is obtained by separating the operator representing the motion of the center of mass from the laboratory Hamiltonian. The internal Hamiltonian used in our non-BO approach is described in the next section. As there is no preferred direction for the system to orient itself in the laboratory coordinate space, the internal Hamiltonian is isotropic (i.e., rotationally invariant). It resembles an atomic BO Hamiltonian. However, as in the atomic Hamiltonian all moving particles are electrons with -1 charges and unit masses (in atomic units), in the internal Hamiltonian some moving particles can be heavier and have positive charges. Like for an atom, the internal Hamiltonian commutes with the operator representing the square of the total angular momentum and its z coordinate, N^2 and N_z. In order to calculate excited molecular states, it is desirable to use, in the calculation, basis functions which are eigenfunctions

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of the two operators. Thus, besides having to be explicitly dependent on the interparticle distances, the basis functions have to possess the right symmetry associated with the total rotational motion of the system.

One of the central issues in the electronic BO calculation is how well it describes the electron-electron (e-e) correlation effects. The electron correlation can be separated into the dynamic and nondynamic correlations. The dynamic correlation is directly related to the Coulombic repulsion between the electrons, which keeps them apart. The nondynamic correlation is due to the electron staying apart due to an electronic excitation of the system or a chemical bond (e.g., a single covalent bond formed by two electrons) between two atoms in the system dissociating and each of the two electrons forming the bond following a different atom. If nuclei and electrons in the calculation are treated on equal footing, nucleus-nucleus (n-n) correlation and nucleus-electron (n-e) correlation need to be represented in the wave function. The e-e, n-e, and n-n correlations are different despite all of them resulting from electrostatic interactions. Due to significantly larger masses of the nuclei, these particles "avoid" each other more than the much lighter electrons. Thus, while the e-e correlations are quite adequately described by ECGs only dependent on the e-e distances in the Gaussian exponent, the n-n correlations, as we have demonstrated with the non-BO calculations of bound states of some small diatomic molecules [6], require preexponential multipliers in the form of non-negative powers of the internuclear distance (the intermolecular distances for molecules with more than two nuclei). We call ECGs with such multipliers "power Gaussians" in this work. The larger the power, the more the nuclei are separated from each other. Inclusion of the zero power assures that the probability of finding the nuclei in a single point in space may not be exactly zero. The multipliers also enable one to describe radial nodes in the wave functions of vibrationally excited states. It is important to note that ECGs used in molecular calculations are single-center Gaussians as only such functions transform according to the irreducible representations of the SO(3) rotation group and can be used to expand wave functions of bound states of the atomlike internal Hamiltonian.

In order to use power ECGs in non-BO calculations of triatomic molecules, the preexponential factor needs to include all three internuclear distances raised to some non-negative powers. Formulas for the Hamiltonian matrix elements for such functions were derived [7], but their computational implementation failed due to the oscillatory nature of these algorithms that caused numerical instabilities in the calculation. After not being able to resolve the problem with the oscillations, we continued searching for an alternative basis which can be used for high-accuracy non-BO calculations of molecules with more than two nuclei. Two such bases have been recently tested in our laboratory. The first one consists of ECGs multiplied by products of sin and cos functions dependent on squares of the interparticle distances [8]. Such functions can correctly describe the decreasing probability of finding two nuclei close to each other. They are also capable of representing radial oscillations of wave functions of vibrationally excited states. The second basis consists of ECGs with complex exponential parameters [9,10]. Based on the initial tests, the latter basis seems to be the most promising.

Before embarking on large-scale non-BO calculations of some triatomic systems—the most interesting being H_3^+, H_3, and HeH_2^+ due to their astrophysical relevance—algorithms for the leading relativistic corrections need to be developed and implemented. Only when these corrections are included in the energy can high-accuracy results be generated for the rovibrational spectra of the mentioned systems. In this work, we derive and test algorithms for calculating the mass-velocity (MV), Darwin (D), and orbit-orbit (OO) interaction corrections to the energy of pure (i.e., rotationless) vibrational states whose wave functions are expanded in terms of complex all-particle ECGs (CECGs). Testing of the algorithms is performed by calculating the relativistic corrections of all 23 bound pure vibrational states of the HD^+ ion and comparing the results with the values obtained before using power ECGs [11]. HD^+ has been used as a model system for comparing high-resolution spectral measurements with high-level theoretical calculations [12,13]. The relativistic corrections taken from Ref. [11] and used in the present testing agree very well with the corrections obtained in the calculations using other methods [12,13].

The algorithms derived in this work are applicable to systems with an arbitrary number of particles. They can be used in non-BO calculations for diatomics, triatomics, as well as systems with more than three nuclei.

II. HAMILTONIAN

We consider an N-particle isolated system with masses $\{M_i\}$ and charges $\{Q_i\}$ in a laboratory Cartesian coordinate system. The laboratory coordinates and the linear momenta of the particles are

$$\mathbf{R} = \begin{bmatrix} \mathbf{R}_1 \\ \mathbf{R}_2 \\ \dots \\ \mathbf{R}_N \end{bmatrix} = \begin{bmatrix} X_1 \\ Y_1 \\ Z_1 \\ \vdots \\ Z_N \end{bmatrix}, \quad \mathbf{P} = \begin{bmatrix} \mathbf{P}_1 \\ \mathbf{P}_2 \\ \dots \\ \mathbf{P}_N \end{bmatrix} = \begin{bmatrix} P_{x1} \\ P_{y1} \\ P_{z1} \\ \vdots \\ P_{zN} \end{bmatrix}. \tag{1}$$

The nonrelativistic laboratory-frame Hamiltonian of the system is

$$H_{\rm nr}(\mathbf{R}) = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2M_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{\|\mathbf{R}_i - \mathbf{R}_j\|}. \tag{2}$$

Next, the $3N$-dimensional problem represented by the above Hamiltonian is reduced to a $(3N-3)$-dimensional problem by eliminating from the laboratory-frame Hamiltonian the operator representing the center-of-mass motion. This elimination is rigorous and achieved by transforming Hamiltonian (2) to a new coordinate system, whose first three coordinates $\mathbf{r}_0$ are the coordinates of the center of mass in the laboratory coordinate frame and the remaining $3N-3$ coordinates are internal coordinates. The internal coordinates, $\mathbf{r}_i$, $i = 1, \dots, N-1$, are coordinates in a Cartesian coordinate system whose center is placed at a selected reference particle (usually the heaviest one). Let $n = N - 1$. In the new coordinate system (2) is

$$H_{\mathrm{nr}}^{\mathrm{tot}}(\mathbf{r}_0,\mathbf{r}) = \left(-\frac{1}{2}\frac{1}{M_{\mathrm{tot}}}\nabla_{\mathbf{r}_0}^2\right) + \left(-\frac{1}{2}\sum_{i}^{n}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 - \frac{1}{2}\sum_{i\neq j}^{n}\frac{1}{m_0}\nabla_{\mathbf{r}_i}^T\nabla_{\mathbf{r}_j} + \sum_{i<j}^{n}\frac{q_iq_j}{r_{ij}} + \sum_{i=1}^{n}\frac{q_0q_i}{r_i}\right), \tag{3}$$

where T denotes the transpose, $q_i = Q_{i+1}$, $\mu_i = \frac{m_0 m_i}{m_0+m_i}$ are the reduced masses, M_{tot} is the total mass of the system, m_0 is the mass of the reference particle, $m_i = M_{i+1}$, $\nabla_{\mathbf{r}_i}$ is the gradient vector expressed in terms of the x_i, y_i, and z_i coordinates of vector $\mathbf{r}_i$, $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\| = \|\mathbf{R}_{i+1} - \mathbf{R}_{j+1}\|$, and $r_{0i} \equiv r_i = \|\mathbf{r}_i\| = \|\mathbf{R}_{i+1} - \mathbf{R}_1\|$. One can call the particles described by the above Hamiltonian "pseudoparticles" because, even though they have the same charges as the original particles, their masses are not the original masses but the reduced masses. As one can see from (3), the separation of the total nonrelativistic laboratory-frame Hamiltonian into the operator representing the kinetic energy of the center-of-mass motion, $H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0)$, and the internal Hamiltonian, $H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r})$, is rigorous:

$$H_{\mathrm{nr}}^{\mathrm{tot}}(\mathbf{r}_0,\mathbf{r}) = H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0) + H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r}). \tag{4}$$

The sum of $H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0)$ and $H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r})$ provides a complete nonrelativistic description of the system. As in this work we are only concerned with the internal bound states of the system, the eigenvalues and eigenfunctions of the internal Hamiltonian are calculated. The internal Hamiltonian can be viewed as describing a system of n pseudoparticles with the masses equal to reduced masses μ_i and charges q_i $(i = 1,\ldots,n)$ moving in the central field of the charge of the reference particle, q_0. The pseudoparticles interact with each other by the Coulombic potential and additionally their motions are coupled through the mass-polarization terms, $-\frac{1}{2}\sum_{i\neq j}^{n}\frac{1}{m_0}\nabla_{\mathbf{r}_i}^T\nabla_{\mathbf{r}_j}$. As mentioned in Sec. I, the internal Hamiltonian (3) is a generalized atomic Hamiltonian due to its spherical symmetry.

III. COMPLEX EXPLICITLY CORRELATED GAUSSIAN FUNCTIONS

The basis functions used in this work are explicitly correlated Gaussian functions with complex parameters. The general form of such functions is

$$\phi_k(\mathbf{r}) = \exp[-\mathbf{r}^T\ \bar{\mathbf{C}}_k\ \mathbf{r}] = \exp[-\mathbf{r}^T\ (\bar{\mathbf{A}}_k + \mathrm{i}\bar{\mathbf{B}}_k)\ \mathbf{r}], \tag{5}$$

where $\bar{\mathbf{A}}_k$ and $\bar{\mathbf{B}}_k$ are real symmetric matrices of the variational exponential parameters. $\bar{\mathbf{A}}_k$ and $\bar{\mathbf{B}}_k$ can be written as $\bar{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3, \bar{\mathbf{B}}_k = \mathbf{B}_k \otimes \mathbf{I}_3$, where $\mathbf{I}_3$ is the 3×3 unit matrix and $\otimes$ denotes the Kronecker product. To ensure square integrability of $\phi_k(\mathbf{r})$, matrix $\mathbf{A}_k$ must be positive definite. To achieve this, $\mathbf{A}_k$ is represented in the Cholesky factored form as $\mathbf{A}_k = \mathbf{L}_k\mathbf{L}_k^T$, where $\mathbf{L}_k$ is an $n\times n$, rank n, lower triangular matrix. $\phi_k(\mathbf{r})$ is square integrable for the $\mathbf{L}_k$ matrix elements being any real numbers.

Relativistic operators

We consider relativistic corrections of the order of α^2. The operators representing the mass-velocity (MV), Darwin (D), and orbit-orbit (OO) interactions in HD$^+$ are [11,14] as follows ($n = 2$).

1. *Mass-velocity term*

$$\langle\phi_k|\ \hat{H}_{\mathrm{MV}}\ |\tilde{\phi}_l\rangle = -\frac{1}{8}\left[\frac{1}{m_0^3}\ \langle\phi_k|\ \left(\sum_{i=1}^{2}\nabla_{\mathbf{r}_i}\right)^4\ |\tilde{\phi}_l\rangle + \sum_{i=1}^{2}\frac{1}{m_i^3}\ \langle\phi_k|\ \nabla_{\mathbf{r}_i}^4\ |\tilde{\phi}_l\rangle\right]. \tag{6}$$

2. *Darwin term*

There are three pair interactions in HD$^+$, i.e., deuteron proton, deuteron electron, and proton electron. In the Dirac-Breit-Pauli relativistic Hamiltonian, which is used in the present work, the Darwin correction describing the interaction of the particle with charge Q, spin I, and mass M with a particle with charge q, spin S, and mass m has the following form [15,16]:

$$\pi\ \frac{3}{2}\ \frac{Qq}{M^2}(g-1)\ (I+\xi)\ \delta^3(\mathbf{r}), \tag{7}$$

where the g factor is the gyromagnetic ratio and parameter ξ is equal to zero for an integer spin and 1/4 for a half-integer spin. HD$^+$ consists of a deuteron $(m_0,q_0,I_0 = 1)$, a proton $(m_1,q_1,I_1 = 1/2)$, and an electron $(m_2,q_2,I_2 = 1/2)$. Neglecting the g factor (as was done by Korobov [17]), the Darwin operator for HD$^+$ is

$$\hat{H}_{\mathrm{D}}(\mathbf{r}) = \frac{\pi}{2}\ \sum_{i=1}^{2}\left(\frac{4}{3}\frac{1}{m_0^2} + \frac{1}{m_i^2}\right)\ q_0q_i\ \delta^3(\mathbf{r}_i) + \frac{\pi}{2}\ \sum_{i=1}^{2}\sum_{j\neq i}^{2}\frac{1}{m_i^2}\ q_iq_j\ \delta^3(\mathbf{r}_{ij}). \tag{8}$$

3. *Orbit-orbit term*

The kl matrix element for the orbit-orbit interaction operator $\hat{H}_{\mathrm{OO}}$ is

$$\begin{aligned}\langle\phi_k|\ \hat{H}_{\mathrm{OO}}(\mathbf{r})\ |\tilde{\phi}_l\rangle &= -\frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{q_0q_j}{m_0m_j}\Bigg[\langle\phi_k|\frac{1}{r_j}\nabla_{\mathbf{r}_i}^T\cdot\nabla_{\mathbf{r}_j}|\tilde{\phi}_l\rangle + \langle\phi_k|\frac{1}{r_j^3}\,\mathbf{r}_j^T\cdot\big(\mathbf{r}_j^T\cdot\nabla_{\mathbf{r}_i}\big)\nabla_{\mathbf{r}_j}|\tilde{\phi}_l\rangle\Bigg]\\ &\quad + \frac{1}{2}\sum_{i=1}^{2}\sum_{j>i}^{2}\frac{q_iq_j}{m_im_j}\Bigg[\langle\phi_k|\frac{1}{r_{ij}}\nabla_{\mathbf{r}_i}^T\cdot\nabla_{\mathbf{r}_j}|\tilde{\phi}_l\rangle + \langle\phi_k|\ \frac{1}{r_{ij}^3}\,\mathbf{r}_{ij}^T\cdot\big(\mathbf{r}_{ij}^T\cdot\nabla_{\mathbf{r}_i}\big)\nabla_{\mathbf{r}_j}|\tilde{\phi}_l\rangle\Bigg].\end{aligned} \tag{9}$$

IV. MATRIX ELEMENTS

In general, the system considered in the calculations may include some groups of identical particles. In the calculation of the wave function expanded in terms of ECGs (5), each Gaussian is transformed with the appropriate permutational symmetry operator. This operator is a product of the permutational symmetry operators each corresponding to a different group of identical particles. For example, for H_2, the permutational symmetry operator is a product of the symmetry operator for the electrons and the symmetry operators for other types of identical particles. Each permutational symmetry operator is a sum of operators permuting the labels of identical particles multiplied by appropriate linear coefficients. The procedure for generating the permutational symmetry operator was described earlier [18]. Each labels-permuting operator is represented by a $3n \times 3n$ permutation matrix. Let us denote by $\underline{\mathbf{P}}$ the permutation matrix representing a particular $\hat{P}$ permutation operator. Then, acting with $\hat{P}$ on ϕ_l, we get

$$\begin{aligned} &\hat{P}\exp[-(\mathbf{r}-\mathbf{s}_l)^T\underline{\mathbf{C}}_l(\mathbf{r}-\mathbf{s}_l)] \\ &\quad = \exp[-(\underline{\mathbf{P}}\mathbf{r}-\mathbf{s}_l)^T\underline{\mathbf{C}}_l(\underline{\mathbf{P}}\mathbf{r}-\mathbf{s}_l)] \\ &\quad = \exp[-(\underline{\mathbf{P}}\mathbf{r}-\underline{\mathbf{P}}\underline{\mathbf{P}}^{-1}\mathbf{s}_l)^T\underline{\mathbf{C}}_l(\underline{\mathbf{P}}\mathbf{r}-\underline{\mathbf{P}}\underline{\mathbf{P}}^{-1}\mathbf{s}_l)] \\ &\quad = \exp[-(\mathbf{r}-\underline{\mathbf{P}}^{-1}\mathbf{s}_l)^T\underline{\mathbf{P}}^T\underline{\mathbf{C}}_l\underline{\mathbf{P}}(\mathbf{r}-\underline{\mathbf{P}}^{-1}\mathbf{s}_l)] \\ &\quad = \exp[-(\mathbf{r}-\tilde{\mathbf{s}}_l)^T\underline{\tilde{\mathbf{C}}}_l(\mathbf{r}-\tilde{\mathbf{s}}_l)], \end{aligned} \tag{10}$$

where $\underline{\tilde{\mathbf{C}}}_l = \underline{\mathbf{P}}^T\underline{\mathbf{C}}_l\underline{\mathbf{P}}$ and $\tilde{\mathbf{s}}_l = \underline{\mathbf{P}}^{-1}\mathbf{s}_l$. The following notation will help keep the expressions more compact:

$$|\tilde{\phi}_l\rangle = \hat{P}|\phi_l\rangle, \tag{11}$$

$$\tilde{L}_k = P^T L_k, \quad \tilde{\bar{\mathbf{A}}}_l = P^T\bar{\mathbf{A}}_l P, \quad \tilde{\bar{\mathbf{B}}}_l = P^T\bar{\mathbf{B}}_l P, \tag{12}$$

$$\bar{\mathbf{A}}_{kl} = \bar{\mathbf{A}}_k + \bar{\mathbf{A}}_l, \quad \tilde{\bar{\mathbf{A}}}_{kl} = \bar{\mathbf{A}}_k + \tilde{\bar{\mathbf{A}}}_l, \tag{13}$$

$$\bar{\mathbf{B}}_{kl} = -\bar{\mathbf{B}}_k + \bar{\mathbf{B}}_l, \quad \tilde{\bar{\mathbf{B}}}_{kl} = -\bar{\mathbf{B}}_k + \tilde{\bar{\mathbf{B}}}_l, \tag{14}$$

and

$$\tilde{\bar{\mathbf{C}}}_{kl} = \bar{\mathbf{C}}_k^* + \tilde{\bar{\mathbf{C}}}_l = \tilde{\bar{\mathbf{A}}}_{kl} + i\tilde{\bar{\mathbf{B}}}_{kl}. \tag{15}$$

Here, P represents the permutation matrix corresponding to some permutation operator $\hat{P}$. As for HD^+, there are no identical particles and the permutational operator is equal to unity.

A. The MV operator

The matrix elements that need to be calculated are

$$\begin{aligned} \langle\phi_k|\hat{H}_{\mathrm{MV}}|\tilde{\phi}_l\rangle = -\frac{1}{8}\Bigg(&\frac{1}{m_0^3}\big\langle\nabla_{\mathbf{r}}^T\mathbf{J}\nabla_{\mathbf{r}}\phi_k\big|\nabla_{\mathbf{r}}^T\mathbf{J}\nabla_{\mathbf{r}}\tilde{\phi}_l\big\rangle \\ &+\sum_{i=1}^{2}\frac{1}{m_i^3}\big\langle\nabla_{\mathbf{r}}^T\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\phi_k\big|\nabla_{\mathbf{r}}^T\bar{\mathbf{J}}_{ii}\nabla_{\mathbf{r}}\tilde{\phi}_l\big\rangle\Bigg), \end{aligned} \tag{16}$$

where we use matrix $\mathbf{J}$ (with no indices), whose elements are all equal to one. Matrix $\mathbf{J}_{ij}$ is defined as

$$\mathbf{J}_{ij} = \begin{cases}\mathbf{E}_{ii}, & \text{if} \quad i = j \\ \mathbf{E}_{ii}+\mathbf{E}_{jj}-\mathbf{E}_{ij}-\mathbf{E}_{ji}, & \text{if} \quad i \neq j,\end{cases} \tag{17}$$

where $\mathbf{E}_{ij}$ is a matrix with one in the i,jth position and zero elsewhere.

Only one type of integral appears in the expression for the $\hat{H}_{\mathrm{MV}}$ matrix elements: $\langle\nabla_{\mathbf{r}}{}^T\bar{\mathbf{D}}\nabla_{\mathbf{r}}\phi_k|\nabla_{\mathbf{r}}{}^T\bar{\mathbf{D}}\nabla_{\mathbf{r}}\bar{\tilde{\phi}}_l\rangle$, where $\bar{\mathbf{D}}$ is either $\bar{\mathbf{J}}$ or $\bar{\mathbf{J}}_{ii}$. To compute it, we express it using the following elementary integrals:

$$\begin{aligned} &\big\langle\nabla_{\mathbf{r}}{}^T\bar{\mathbf{D}}\nabla_{\mathbf{r}}\phi_k\big|\nabla_{\mathbf{r}}{}^T\bar{\mathbf{D}}\nabla_{\mathbf{r}}\tilde{\phi}_l\big\rangle \\ &\quad = 36\ \mathrm{Tr}\,[\mathbf{C}_k^\dagger\mathbf{D}]\ \mathrm{Tr}\,[\tilde{\mathbf{C}}_l\mathbf{D}]\langle\phi_k|\tilde{\phi}_l\rangle \\ &\qquad - 24\ \mathrm{Tr}\,[\tilde{\mathbf{C}}_k^\dagger\mathbf{D}]\langle\phi_k|\mathbf{r}^T\tilde{\bar{\mathbf{C}}}_l\overline{\mathbf{D}\tilde{\mathbf{C}}}_l\mathbf{r}|\tilde{\phi}_l\rangle \\ &\qquad - 24\ \mathrm{Tr}\,[\tilde{\mathbf{C}}_l\mathbf{D}]\langle\phi_k|\mathbf{r}^T\bar{\mathbf{C}}_k^\dagger\overline{\mathbf{D}\mathbf{C}}_k^\dagger\mathbf{r}|\tilde{\phi}_l\rangle \\ &\qquad + 16\langle\phi_k|\mathbf{r}^T\bar{\mathbf{C}}_k^\dagger\overline{\mathbf{D}\mathbf{C}}_k^\dagger\mathbf{r}\ \mathbf{r}^T\tilde{\bar{\mathbf{C}}}_l\overline{\mathbf{D}\tilde{\mathbf{C}}}_l\mathbf{r}|\tilde{\phi}_l\rangle. \end{aligned} \tag{18}$$

B. The orbit-orbit interaction operator

The matrix notation of the orbit-orbit interaction operator is (for details, see [19])

$$\langle\phi_k|\hat{H}_{oo}(\mathbf{r})|\tilde{\phi}_l\rangle = -\frac{1}{2}\sum_{i=1}^{2}\frac{q_0q_i}{m_0m_{i+1}}\langle\phi_k|\frac{1}{r_i}\nabla^T\bar{\mathbf{E}}_{ii}\nabla - (\mathbf{r}^T\bar{\mathbf{E}}_{ii})^\alpha\left(\nabla^T\bar{\mathbf{E}}_{ii}\frac{1}{r_i}\right)^\beta(\bar{\mathbf{E}}_{ii}\nabla)_\beta(\bar{\mathbf{E}}_{ii}\nabla)_\alpha|\tilde{\phi}_l\rangle \tag{19}$$

$$-\frac{1}{2}\sum_{i=1}^{2}\sum_{j\neq i}^{2}\frac{q_0q_i}{m_0m_{i+1}}\langle\phi_k|\frac{1}{r_i}\nabla^T\bar{\mathbf{E}}_{ij}\nabla - (\mathbf{r}^T\bar{\mathbf{E}}_{ii})^\alpha\left(\nabla^T\bar{\mathbf{E}}_{ij}\frac{1}{r_i}\right)^\beta(\bar{\mathbf{E}}_{jj}\nabla)_\beta(\bar{\mathbf{E}}_{ii}\nabla)_\alpha|\tilde{\phi}_l\rangle \tag{20}$$

$$+\frac{1}{2}\sum_{i=1}^{n-1}\sum_{j>i}^{2}\frac{q_iq_j}{m_{i+1}m_{j+1}}\langle\phi_k|\frac{1}{r_{ij}}\nabla^T\bar{\mathbf{E}}_{ij}\nabla + [\mathbf{r}^T(\bar{\mathbf{E}}_{ij}-\bar{\mathbf{E}}_{jj})]^\alpha\left(\nabla^T\bar{\mathbf{E}}_{ji}\frac{1}{r_{ij}}\right)^\beta(\bar{\mathbf{E}}_{ii}\nabla)_\beta(\bar{\mathbf{E}}_{jj}\nabla)_\alpha|\tilde{\phi}_l\rangle. \tag{21}$$

To simplify the expression for the $\hat{H}_{oo}(\mathbf{r})$ expectation value, we use the following general integrals for the three terms that appear in it:

$$\langle\phi_k|\frac{1}{r_g}\nabla^T\ \bar{\mathbf{B}}\ \nabla|\tilde{\phi}_l\rangle - \langle\phi_k|(\mathbf{r}^T\ \bar{\mathbf{K}})^\alpha\left(\nabla^T\bar{\mathbf{D}}\ \frac{1}{r_g}\right)^\beta(\bar{\mathbf{F}}\ \nabla)_\beta(\bar{\mathbf{G}}\ \nabla)_\alpha|\tilde{\phi}_l\rangle$$

$$\begin{array}{llllll}
\text{for term (19):} & g=i & \overline{\mathbf{B}}=\overline{\mathbf{E}}_{ii} & \overline{\mathbf{K}}=\overline{\mathbf{E}}_{ii} & \overline{\mathbf{D}}=\overline{\mathbf{E}}_{ii} & \overline{\mathbf{F}}=\overline{\mathbf{E}}_{ii} \quad \overline{\mathbf{G}}=\overline{\mathbf{E}}_{ii}, \\
\text{for term (20):} & g=i & \overline{\mathbf{B}}=\overline{\mathbf{E}}_{ij} & \overline{\mathbf{K}}=\overline{\mathbf{E}}_{ii} & \overline{\mathbf{D}}=\overline{\mathbf{E}}_{ij} & \overline{\mathbf{F}}=\overline{\mathbf{E}}_{jj} \quad \overline{\mathbf{G}}=\overline{\mathbf{E}}_{ii}, \\
\text{for term (21):} & g=ij & \overline{\mathbf{B}}=\overline{\mathbf{E}}_{ij} & \overline{\mathbf{K}}=(\overline{\mathbf{E}}_{ij}-\overline{\mathbf{E}}_{jj}) & \overline{\mathbf{D}}=\overline{\mathbf{E}}_{ji} & \overline{\mathbf{F}}=\overline{\mathbf{E}}_{ii} \quad \overline{\mathbf{G}}=\overline{\mathbf{E}}_{jj},
\end{array} \tag{22}$$

where

$$\langle\phi_k|\frac{1}{r_g}\ \nabla^T\ \overline{\mathbf{B}}\ \nabla\ |\tilde{\phi}_l\rangle = +4\langle\phi_k|\frac{1}{r_g}(\mathbf{r}^T\ \tilde{\overline{\mathbf{C}}}_l\ \overline{\mathbf{B}}\ \tilde{\overline{\mathbf{C}}}_l\ \mathbf{r})\ |\tilde{\phi}_l\rangle - 6\ \mathrm{Tr}\ [\tilde{\mathbf{C}}_l\mathbf{B}]\langle\phi_k|\frac{1}{r_g}|\tilde{\phi}_l\rangle,$$

$$\begin{aligned}
&\langle\phi_k|\ (\mathbf{r}^T\ \overline{\mathbf{K}})^\alpha\left(\nabla^T\ \overline{\mathbf{D}}\ \frac{1}{r_g}\right)^\beta(\overline{\mathbf{F}}\ \nabla)_\beta(\overline{\mathbf{G}}\ \nabla)_\alpha|\tilde{\phi}_l\rangle \\
&= +8\langle\phi_k|\frac{1}{r_g}\ (\mathbf{r}^T\ \overline{\mathbf{K}}\ \overline{\mathbf{G}}\ \tilde{\overline{\mathbf{C}}}_l\ \mathbf{r})(\mathbf{r}^T\overline{\mathbf{C}}_k^\dagger\ \overline{\mathbf{D}}\ \overline{\mathbf{F}}\ \tilde{\overline{\mathbf{C}}}_l\ \mathbf{r})\ |\tilde{\phi}_l\rangle - 4\langle\phi_k|\frac{1}{r_g}(\mathbf{r}^T\overline{\mathbf{C}}_k^\dagger\ \overline{\mathbf{D}}\ \overline{\mathbf{F}}\ \tilde{\overline{\mathbf{C}}}_l\ \overline{\mathbf{G}}^T\ \overline{\mathbf{K}}^T\ \mathbf{r})|\tilde{\phi}_l\rangle \\
&\quad - 4\langle\phi_k|\frac{1}{r_g}\ (\mathbf{r}^T\ \tilde{\overline{\mathbf{C}}}_l\ \overline{\mathbf{G}}^T\ \overline{\mathbf{K}}^T\ \overline{\mathbf{D}}\ \overline{\mathbf{F}}\ \tilde{\overline{\mathbf{C}}}_l\ \mathbf{r})\ |\tilde{\phi}_l\rangle + 6\ \mathrm{Tr}\ [\tilde{\mathbf{C}}_l\ \mathbf{G}^T\ \mathbf{K}^T\ \mathbf{D}\ \mathbf{F}\ ]\langle\phi_k|\frac{1}{r_g}|\tilde{\phi}_l\rangle - 4\langle\phi_k|\ \frac{1}{r_g}[(\mathbf{r}^T\ \overline{\mathbf{K}}\ \overline{\mathbf{G}}\ \tilde{\overline{\mathbf{C}}}_l\ \overline{\mathbf{D}}\ \overline{\mathbf{F}}\ \tilde{\overline{\mathbf{C}}}_l\mathbf{r}) \\
&\quad + (\mathbf{r}^T\ \overline{\mathbf{K}}\ \overline{\mathbf{G}}\ \tilde{\overline{\mathbf{C}}}_l\ \overline{\mathbf{F}}^T\ \overline{\mathbf{D}}^T\ \tilde{\overline{\mathbf{C}}}_l\ \mathbf{r})]|\tilde{\phi}_l\rangle - 12\ \mathrm{Tr}\ [\mathbf{D}\ \mathbf{F}\ \tilde{\mathbf{C}}_l]\langle\phi_k|\frac{1}{r_g}(\mathbf{r}^T\overline{\mathbf{K}}\ \overline{\mathbf{G}}\ \tilde{\overline{\mathbf{C}}}_l\mathbf{r})|\tilde{\phi}_l\rangle + 8\langle\phi_k|\frac{1}{r_g}(\mathbf{r}^T\ \overline{\mathbf{K}}\ \overline{\mathbf{G}}\ \tilde{\overline{\mathbf{C}}}_l\mathbf{r})(\mathbf{r}^T\tilde{\overline{\mathbf{C}}}_l\ \overline{\mathbf{D}}\ \overline{\mathbf{F}}\ \tilde{\overline{\mathbf{C}}}_l\mathbf{r})|\tilde{\phi}_l\rangle.
\end{aligned}$$

C. The integral

The following well-known Gaussian integral is used in the derivation:

$$\int_{-\infty}^{+\infty} d^n x\ \ \exp[-x'Cx + y'x] = \frac{\pi^{n/2}}{|C|^{1/2}}\exp\left[\frac{1}{4}y'C^{-1}y\right]. \tag{23}$$

The integration in (23) is over n variables and x is an n-component vector of these variables. y is a constant vector, $n\times n$ matrix C is assumed to be symmetric, and its real part is positive definite. Also, here and everywhere below, by the square root one should understand its principal value (i.e., the root whose real part is greater than zero).

1. *Overlap integral*

For the derivation of this integral, see [9]. The integral is

$$\langle\phi_k|\tilde{\phi}_l\rangle \equiv \langle\phi_k|\hat{P}|\phi_l\rangle = \pi^{3n/2}|\tilde{\mathbf{C}}_{kl}|^{-3/2}, \tag{24}$$

$$\mathrm{S}_{kl} = \frac{\langle\phi_k|\tilde{\phi}_l\rangle}{(\langle\phi_k|\phi_k\rangle\langle\phi_l|\phi_l\rangle)^{1/2}} = \frac{(|\mathbf{C}_{kk}|^{3/2}|\mathbf{C}_{ll}|^{3/2})^{1/2}}{|\tilde{\mathbf{C}}_{kl}|^{3/2}} = 2^{3n/2}\left(\frac{||\mathbf{L}_k||\ ||\mathbf{L}_l||}{|\tilde{\mathbf{C}}_{kl}|}\right)^{3/2}. \tag{25}$$

2. *Elementary integrals*

Now we present formulas for the elementary integrals used in the equations for the above-described matrix elements. For more details concerning the derivation of the integrals, see [20,21].

$$\langle\phi_k|(\mathbf{r}^T\overline{\mathbf{X}}\ \mathbf{r})|\tilde{\phi}_l\rangle = \mathrm{S}_{kl}\ \ \tfrac{3}{2}\ \mathrm{Tr}\big[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\ \big], \tag{26}$$

$$\langle\phi_k|(\mathbf{r}^T\overline{\mathbf{X}}\ \mathbf{r})\big(\mathbf{r}^T\overline{\mathbf{Y}}\ \mathbf{r}\big)|\tilde{\phi}_l\rangle = \mathrm{S}_{kl}\ \big\{\tfrac{9}{4}\ \mathrm{Tr}\ \big[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\big]\ \mathrm{Tr}\ \big[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{Y}\big] + \tfrac{3}{2}\ \ \mathrm{Tr}\ \big[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\ \tilde{\mathbf{C}}_{kl}^{-1}\mathbf{Y}\big]\big\}. \tag{27}$$

Using the designation $g = ii$ (or, more precisely, $g = i$ when it appears in r_g and $g = ii$ when it appears in $\mathbf{J}_g$) or ij, we get

$$\langle\phi_k|\ \frac{1}{r_g}\ |\tilde{\phi}_l\rangle = \mathrm{S}_{kl}\ \frac{2}{\sqrt{\pi}}\ \ \mathrm{Tr}\ \big[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{J}_g\big]^{-1/2}, \tag{28}$$

$$\langle\phi_k|(\mathbf{r}^T\overline{\mathbf{X}}\mathbf{r})\ \frac{1}{r_g}\ |\tilde{\phi}_l\rangle = \langle\phi_k|\ \frac{1}{r_g}\ |\tilde{\phi}_l\rangle\ \frac{1}{2}\left[3\ \mathrm{Tr}\ \big[\mathbf{X}\tilde{\mathbf{C}}_{kl}^{-1}\big] - \ \frac{\mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\ \tilde{\mathbf{C}}_{kl}^{-1}\big]}{\mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\big]}\right], \tag{29}$$

$$\langle\phi_k|\frac{1}{r_g}\ (\mathbf{r}^T\overline{\mathbf{X}}\mathbf{r})(\mathbf{r}^T\overline{\mathbf{Y}}\mathbf{r})\ |\tilde{\phi}_l\rangle = \langle\phi_k|\ \frac{1}{r_g}\ |\tilde{\phi}_l\rangle\ \frac{1}{4}\ \Big\{9\ \mathrm{Tr}\ \big[\mathbf{X}\tilde{\mathbf{C}}_{kl}^{-1}\big]\ \ \mathrm{Tr}\ \big[\mathbf{Y}\tilde{\mathbf{C}}_{kl}^{-1}\big] + 6\ \mathrm{Tr}\ \big[\mathbf{X}\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{Y}\tilde{\mathbf{C}}_{kl}^{-1}\big] \tag{30}$$

$$- \frac{1}{\mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\big]}\big(3\ \mathrm{Tr}\ \big[\mathbf{X}\tilde{\mathbf{C}}_{kl}^{-1}\big]\ \mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{Y}\tilde{\mathbf{C}}_{kl}^{-1}\big] + 3\ \mathrm{Tr}\ \big[\mathbf{Y}\tilde{\mathbf{C}}_{kl}^{-1}\big]\ \mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\tilde{\mathbf{C}}_{kl}^{-1}\big]$$

$$+4\ \ \mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{Y}\tilde{\mathbf{C}}_{kl}^{-1}\big]\big) \tag{31}$$

$$+ \frac{1}{\mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\big]^2}\ 3\ \ \mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{X}\ \tilde{\mathbf{C}}_{kl}^{-1}\big]\ \mathrm{Tr}\ \big[\mathbf{J}_g\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{Y}\ \tilde{\mathbf{C}}_{kl}^{-1}\big]\Big\}. \tag{32}$$

TABLE I. The convergence of the total nonrelativistic non-BO energies of the pure vibrational states of HD$^+$. The results marked with * are taken from Ref. [11]. All energy values are given in a.u. (hartrees).

v	Basis	Energy	v	Basis	Energy	v	Basis	Energy	v	Basis	Energy
0	900	−0.5978979683912	1	900	−0.5891818289282	2	900	−0.5809036983037	3	900	−0.5730505414248
	1100	−0.5978979685138		1100	−0.5891818293204		1100	−0.5809036995907		1100	−0.5730505449747
	1300	−0.5978979685585		1300	−0.5891818294385		1300	−0.5809036999147		1300	−0.5730505458830
	*4000	−0.5978979685771		*5000	−0.5891818295415		*4000	−0.5809037002014		*4000	−0.5730505464509
4	900	−0.5656110283385	5	900	−0.5585754944135	6	900	−0.5519358963488	7	900	−0.5456858304071
	1100	−0.5656110377595		1100	−0.5585755123631		1100	−0.5519359315109		1100	−0.5456858832782
	1300	−0.5656110404136		1300	−0.5585755179626		1300	−0.5519359435920		1300	−0.5456859064213
	*4000	−0.5656110420151		*4000	−0.5585755206666		*4000	−0.5519359486245		*4000	−0.5456859149958
8	900	−0.5398204968565	9	900	−0.5343367888427	10	900	−0.5292332938131	11	900	−0.5245104708403
	1100	−0.5398205841104		1100	−0.5343369274054		1100	−0.5292335367206		1100	−0.5245107785210
	1300	−0.5398206258429		1300	−0.5343369896236		1300	−0.5292335976010		1300	−0.5245108605721
	*4000	−0.5398206405530		*4000	−0.5343370131078		*4000	−0.5292336347464		*4000	−0.5245109096420
12	900	−0.5201704915092	13	900	−0.5162177565392	14	900	−0.5126589689627	15	900	−0.5095030544577
	1100	−0.5201709540191		1100	−0.5162184418657		1100	−0.5126598249150		1100	−0.5095042075422
	1300	−0.5201710800433		1300	−0.5162186121525		1300	−0.5126600498905		1300	−0.5095044653161
	*4000	−0.5201711438355		*4000	−0.5162187088779		*5000	−0.5126601912543		*5000	−0.5095046474123
16	900	−0.5067619132317	17	900	−0.5044503592932	18	900	−0.5025865108464	19	900	−0.5011923477510
	1100	−0.5067632927475		1100	−0.5044519869695		1100	−0.5025884884742		1100	−0.5011940209047
	1300	−0.5067636279441		1300	−0.5044524069436		1300	−0.5025888978524		1300	−0.5011944645923
	*6000	−0.5067638738368		*6000	−0.5044526917472		*6000	−0.5025892273423		*7000	−0.5011947942236
20	900	−0.5002900763374	21	900	−0.4999094630930	22	900	−0.4998654605144			
	1100	−0.5002916950979		1100	−0.4999100692534		1100	−0.4998656818779			
	1300	−0.5002921103721		1300	−0.4999102425427		1300	−0.4998657400793			
	*7000	−0.500292453636		*7000	−0.4999103594832		*7000	−0.4998657783078			

3. *Dirac δ function*

In calculating the matrix element of the three-dimensional Dirac δ function, we use the formula

$$\delta(\mathbf{a}^T\mathbf{r}-\boldsymbol{\xi}) = \delta(a_1\mathbf{r}_1 + a_2\mathbf{r}_2 + \cdots + a_n\mathbf{r}_n - \boldsymbol{\xi}),$$

where $\mathbf{a}$ is a real n-component vector and $\boldsymbol{\xi}$ is some real three-dimensional parameter [9]. Using the following representation of the δ function:

$$\delta(\mathbf{a}^T\mathbf{r}-\boldsymbol{\xi}) = \lim_{\beta\to\infty}\left(\frac{\beta}{\pi}\right)^{3/2}\exp[-\beta(\mathbf{a}^T\mathbf{r}-\boldsymbol{\xi})^2] \tag{33}$$

and formula (23), we get

$$\begin{aligned}
&\langle\phi_k|\delta(\mathbf{a}^T\mathbf{r}-\boldsymbol{\xi})|\tilde{\phi}_l\rangle \\
&= \lim_{\beta\to\infty}\left(\frac{\beta}{\pi}\right)^{3/2}\langle\phi_k|\exp[-\beta\mathbf{r}^T(\mathbf{a}\mathbf{a}^T)\mathbf{r} \\
&\quad + 2\beta\mathbf{a}^T\mathbf{r}\boldsymbol{\xi} - \beta\boldsymbol{\xi}^T\boldsymbol{\xi}]|\tilde{\phi}_l\rangle \qquad (34)\\
&= \frac{\mathrm{S}_{kl}}{\pi^{3/2}\ \mathrm{Tr}\left[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{a}\mathbf{a}^T\right]^{3/2}}\exp\left\{-\frac{\boldsymbol{\xi}^T\boldsymbol{\xi}}{\mathrm{Tr}\left[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{a}\mathbf{a}^T\right]}\right\}. \qquad (35)
\end{aligned}$$

The above matrix elements are obtained by setting $\mathbf{a}$ as $\mathbf{a} = \mathbf{j}^i$ or $\mathbf{a} = \mathbf{j}^j - \mathbf{j}^i$, where $\mathbf{j}^i$ is an n-component vector whose ith component is equal to one, while all others are equal to zero. One should note that $\mathbf{r}_{ij} = (\mathbf{j}^j - \mathbf{j}^i)^T\mathbf{r}$, $\mathbf{r}_i = (\mathbf{j}^i)^T\mathbf{r}$, and also $(\mathbf{j}^j - \mathbf{j}^i)(\mathbf{j}^j - \mathbf{j}^i)^T = \mathbf{J}_{ij}$ for $i \neq j$ and $\mathbf{j}^i(\mathbf{j}^i)^T = \mathbf{J}_{ii}$ for $i = j$. With that, we have

$$\begin{aligned}
&\langle\phi_k|\delta(\mathbf{r}_{ij}-\boldsymbol{\xi})|\tilde{\phi}_l\rangle \\
&= \frac{\mathrm{S}_{kl}}{\pi^{3/2}\ \mathrm{Tr}\left[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{J}_{ij}\right]^{3/2}}\exp\left\{-\frac{\boldsymbol{\xi}^T\boldsymbol{\xi}}{\mathrm{Tr}\left[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{J}_{ij}\right]}\right\}, \qquad (36)\\
&\langle\phi_k|\delta(\mathbf{r}_{i}-\boldsymbol{\xi})|\tilde{\phi}_l\rangle \\
&= \frac{\mathrm{S}_{kl}}{\pi^{3/2}\ \mathrm{Tr}\left[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{J}_{ii}\right]^{3/2}}\exp\left\{-\frac{\boldsymbol{\xi}^T\boldsymbol{\xi}}{\mathrm{Tr}\left[\tilde{\mathbf{C}}_{kl}^{-1}\mathbf{J}_{ii}\right]}\right\}. \qquad (37)
\end{aligned}$$

V. NUMERICAL TEST

The algorithms for the relativistic corrections derived in this work are implemented on a parallel computer platform using FORTRAN90 and message passing interface (MPI). The implementation is general and can be applied to an arbitrary number of particles. The computational costs for calculation of the matrix elements with CECGs and with the power ECGs are similar. The solving of the secular equation for CECGs takes somewhat more time than for the power ECGs, as it involves diagonalization of the complex Hamiltonian and overlap matrices.

The test calculations are performed for all 23 bound rotationless vibrational states of the HD$^+$ ion. HD$^+$ has been chosen because very accurate results concerning the leading relativistic calculations for this system were calculated in our recent work [11] using real ECGs with preexponential multipliers being even non-negative powers $2m_k$ of the internuclear distance r_1:

$$\phi_k(\mathbf{r}) = r_1^{2m_k} \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}]. \tag{38}$$

The CECG basis set for each state is generated by a growing process involving adding new functions in subsets of 20, variationally optimizing their nonlinear parameters (i.e., the elements of the L_k and B_k matrices), and then reoptimizing the parameters of all CECGs in the basis set. In the optimization and reoptimization steps, one basis function at a time is optimized and the procedure cycles over all functions several times to achieve the desired level of the energy convergence. The analytical energy gradient determined with respect to the optimization parameters is used to accelerate the optimization process.

The maximum number of the basis functions generated for each state is 1300 (this is 300 more for states with $v = 8$–22 than presented in our previous CECG for on HD$^+$ [10]). The total energies obtained with this number of CECGs, as well as the energies obtained with 1100 and 900 CECGs obtained in the present calculation for all 23 bound vibrational states corresponding to the zero total angular momentum quantum number, are show in Table I. The energies are compared with the energies obtained with real ECGs [Eq. (38)]. The number of the real ECGs used for each state is also shown in the table. As one can see, this number increases from 4000 for the lowest state to 7000 for the top state. As expected, the CECG energies are slightly higher than the corresponding ECG energies and, as only 1300 CECGs are used for all states, the energy gap between the CECG and ECG energies increases with the vibrational excitation. For the $v = 0$ state, the difference between the two energies appears at the 11th significant figure, but for the highest $v = 22$ state, the two energies already differ at the eighth significant figure.

The wave functions obtained with 900, 1100, and 1300 basis functions for each state are used to calculate the MV, D, and OO relativistic corrections as the first-order perturbation-theory energy corrections. The results are shown in Table II. The

TABLE II. Expectation values of the operators representing the leading relativistic corrections: mass velocity (MV), Darwin (D), and orbit orbit (OO). The results marked with * are taken from Ref. [11]. All energy values are given in a.u. (hartrees).

v	Basis	MV	D	OO	v	Basis	MV	D	OO	v	Basis	MV	D	OO
0	900	−0.7874	0.6508	−4.784E-04	1	900	−0.7696	0.6388	−4.669E-04	2	900	−0.7531	0.6217	−4.564E-04
	1100	−0.7874	0.6508	−4.784E-04		1100	−0.7698	0.6359	−4.669E-04		1100	−0.7532	0.6218	−4.564E-04
	1300	−0.7875	0.6508	−4.784E-04		1300	−0.7698	0.6359	−4.669E-04		1300	−0.7533	0.6219	−4.564E-04
	*4000	−0.7873	0.6507	−4.784E-04		*5000	−0.7697	0.6358	−4.669E-04		*4000	−0.7533	0.6219	−4.564E-04
3	900	−0.7378	0.6086	−4.468E-04	4	900	−0.7234	0.5962	−4.380E-04	5	900	−0.7101	0.5847	−4.300E-04
	1100	−0.7379	0.6087	−4.468E-04		1100	−0.7236	0.5964	−4.380E-04		1100	−0.7105	0.5851	−4.300E-04
	1300	−0.7380	0.6088	−4.468E-04		1300	−0.7237	0.5966	−4.380E-04		1300	−0.7106	0.5852	−4.300E-04
	*4000	−0.7378	0.6087	−4.468E-04		*4000	−0.7237	0.5966	−4.380E-04		*4000	−0.7105	0.5852	−4.300E-04
6	900	−0.6977	0.5739	−4.227E-04	7	900	−0.6863	0.5638	−4.163E-04	8	900	−0.6758	0.5545	−4.105E-04
	1100	−0.6982	0.5744	−4.227E-04		1100	−0.6867	0.5643	−4.163E-04		1100	−0.6763	0.5552	−4.105E-04
	1300	−0.6983	0.5746	−4.227E-04		1300	−0.6871	0.5647	−4.163E-04		1300	−0.6766	0.5555	−4.105E-04
	*4000	−0.6983	0.5746	−4.227E-04		*4000	−0.6872	0.5649	−4.163E-04		*4000	−0.6768	0.5557	−4.105E-04
9	900	−0.6666	0.5461	−4.055E-04	10	900	−0.6573	0.5377	−4.013E-04	11	900	−0.6500	0.5309	−3.977E-04
	1100	−0.6671	0.5468	−4.055E-04		1100	−0.6584	0.5389	−4.013E-04		1100	−0.6510	0.5319	−3.977E-04
	1300	−0.6674	0.5472	−4.055E-04		1300	−0.6589	0.5395	−4.013E-04		1300	−0.6512	0.5324	−3.977E-04
	*4000	−0.6676	0.5475	−4.055E-04		*4000	−0.6590	0.5397	−4.013E-04		*4000	−0.6516	0.5329	−3.977E-04
12	900	−0.6429	0.5242	−3.948E-04	13	900	−0.6365	0.5180	−3.927E-04	14	900	−0.6313	0.5128	−3.913E-04
	1100	−0.6435	0.5250	−4.948E-04		1100	−0.6374	0.5191	−3.927E-04		1100	−0.6323	0.5139	−3.913E-04
	1300	−0.6442	0.5258	−4.948E-04		1300	−0.6384	0.5201	−3.927E-04		1300	−0.6332	0.5149	−3.913E-04
	*4000	−0.6442	0.5260	−3.949E-04		*4000	−0.6389	0.5209	−3.927E-04		*5000	−0.6338	0.5158	−3.913E-04
15	900	−0.6267	0.5080	−3.906E-04	16	900	−0.6232	0.5041	−3.907E-04	17	900	−0.6199	0.5002	−3.914E-04
	1100	−0.6281	0.5095	−3.906E-04		1100	−0.6240	0.5050	−3.907E-04		1100	−0.6207	0.5012	−3.914E-04
	1300	−0.6287	0.5103	−3.907E-04		1300	−0.6250	0.5060	−3.907E-04		1300	−0.6225	0.5029	−3.914E-04
	*5000	−0.6295	0.5112	−3.907E-04		*6000	−0.6260	0.5073	−3.907E-04		*6000	−0.6235	0.5042	−3.915E-04
18	900	−0.6171	0.4966	−3.926E-04	19	900	−0.6185	0.4968	−3.932E-04	20	900	−0.6187	0.4953	−3.863E-04
	1100	−0.6195	0.4991	−3.926E-04		1100	−0.6195	0.4977	−3.933E-04		1100	−0.6204	0.4972	−3.864E-04
	1300	−0.6210	0.5005	−3.926E-04		1300	−0.6204	0.4988	−3.933E-04		1300	−0.6211	0.4981	−3.864E-04
	*6000	−0.6218	0.5017	−3.927E-04		*7000	−0.6213	0.5000	−3.933E-04		*7000	−0.6218	0.4992	−3.865E-04
21	900	−0.6220	0.4974	−2.966E-04	22	900	−0.6234	0.4987	−2.747E-04					
	1100	−0.6223	0.4980	−2.972E-04		1100	−0.6238	0.4990	−2.751E-04					
	1300	−0.6229	0.4986	−2.974E-04		1300	−0.6239	0.4992	−2.752E-04					
	*7000	−0.6235	0.4992	−2.975E-04		*7000	−0.6242	0.4995	−2.752E-04					
	$\mathrm{D}+\mathrm{H}^+$	−0.62432	0.49959	$-2.722\ 10^{-4}$										
	$\mathrm{D}^+ + \mathrm{H}$	−1.2483	0.49918	$-5.437\ 10^{-4}$										

results are compared with the results obtained with ECGs (38). As for the total energies, the agreement between the CECG and ECG results becomes progressively worse, but, even in the worse case, it is less than one in the third significant digit. It is remarkable that for the OO correction, the CECG calculations reproduce virtually all four significant figures of the results obtained in the ECG calculations. In conclusion, we can say that the derived algorithms and their computational implementation are correct.

VI. SUMMARY

In our view, the development of methods employing complex explicitly correlated n-particle Gaussian functions for molecular non-BO calculations is a promising approach for extending the calculations of bound rovibrational states to molecular systems with more than two nuclei. These functions are very efficient in describing the highly correlated motion of particles with widely different masses and charges interacting with Coulombic potentials. The focus of the present work is the development of algorithms for calculating the leading relativistic corrections using the first-order perturbation theory. The tests performed of all 23 bound vibrational states of the HD^+ ion corresponding to the zero total rotational quantum number show excellent agreement with the previous high-accuracy results obtained with the real ECGs involving non-negative even powers of the internuclear distance (i.e., in the case of HD^+, the p-d distance) as preexponential multipliers. The relativistic correction is indispensable in high-accuracy calculations of rovibrational transition energies. The algorithms developed in this work and their computation implementation are general and can be applied to an arbitrary number of particles. Applications of the algorithms in non-BO calculations of such systems as H_3^+, HeH_2^+, etc. are forthcoming.

ACKNOWLEDGMENT

This work was supported by the Polish National Science Centre, Grant No. DEC-2013/10/E/ST4/00033, and by the National Science Foundation, Grant No. IIA-1444127.

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