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Research paper

Implementation of explicitly correlated complex Gaussian functions in calculations of molecular rovibrational $J = 1$ states without Born-Oppenheimer approximation

Erik M. Chavez[a], Sergiy Bubin[b], Ludwik Adamowicz[c,d,*]

[a] Department of Chemistry and Biochemistry, University of Arizona, Tucson, AZ 85721, USA
[b] Department of Physics, School of Science and Technology, Nazarbayev University, Astana 010000, Kazakhstan
[c] Department of Chemistry and Biochemistry and Department of Physics, University of Arizona, Tucson, AZ 85721, USA
[d] Interdisciplinary Center for Modern Technologies, Nicolaus Copernicus University, ul. Wileńska 4, Toruń, PL 87-100, Poland

HIGHLIGHTS

- A new non-Born-Oppenheimer molecular method is presented and used to calculate all 23 bound states of HD^+ with L = 1.

ABSTRACT

In our previous work (Bubin et al., 2016) it was established that complex explicitly-correlated one-center all-particle Gaussian functions (CECGs) provide an effective basis set for very accurate non-relativistic molecular non-Born-Oppenheimer (non-BO) calculations for vibrational ground and excited states corresponding to the rotational ground state. In this work we advance the molecular CECGs approach further by implementing and testing the algorithms for calculating the vibrational states corresponding to the first rotational excited state (the $J = 1$ state). The test concerns all bound $J = 1$ rovibrational states of the HD^+ ion.

1. Introduction

In recent years there has been interest is quantum mechanical calculations of molecular bound ground and excited states without assuming the Born-Oppenheimer (BO) approximation [1–3]. There are at least two reasons why such calculations are interesting. The first is related to more accurately calculate the molecular rovibrational and electronic spectra. When the BO approximation is not assumed, the wave functions and the corresponding nonrelativistic energy levels of the molecule explicitly include effects originating from the finite mass of the nuclei and from the coupling of the motions of the nuclei and the electrons. If such non-BO wave functions are used to calculate relativistic and QED corrections, these corrections also directly include the finite-nuclear-mass (FNM) effects, i.e. the so-called recoil effects. We have showed that such an approach can produce results whose accuracy match the accuracy of the most accurate experimental measurements [3]. The second reason for carrying out the non-BO molecular calculations stems from the interest in describing properties and structures of molecules by calculations where all particles forming the system are treated on equal footing. With that the molecular structure, the dipole moment, the polarizabilities, etc., are obtained as expectation values of operators representing these properties and, for molecules containing identical nuclei, indistinguishability principle leads to interesting effects not present when the BO approximation is assumed.

Despite both being based on the principles of quantum mechanics there are significant differences between BO and non-BO calculations of molecular energies and the corresponding wave functions. The former involve separate calculations of the electronic wave functions and the corresponding energies 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 rovibrational states of the molecule. In non-BO calculations the nuclei and the electrons forming the molecule are treated on an 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. At the non-relativistic level, as the Hamiltonian used to calculate the internal states of the system commutes with the operators representing the square of the total angular momentum operator and it z coordinate (quantum numbers that quantize these quantities are good quantum numbers), the wave functions are atom-like (i.e. they should transform

* Corresponding author.
E-mail address: ludwik@email.arizona.edu (L. Adamowicz).

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according to the irreducible representations of the SO(3) rotation group).

The starting point of the approach we have used in the non-BO molecular calculations is the non-relativistic Hamiltonian dependent on laboratory-frame Cartesian coordinates of all particles forming the system. As this Hamiltonian includes the relative motion of the particles around the center of mass of the system (here termed the internal motion), as well the translational motion of the center of mass in space, the two motions have to be separated so the calculation only focuses on system's "internal" bound states. 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.

One of the central issues in non-BO calculations is the selection of the basis functions for expanding the spatial part of the wave function. In this work we continue to advance this subject. Our ultimate goal in the development is to extend the non-BO calculations of rovibrational states to molecules with more than two nuclei. The present work is a part of this effort.

2. Hamiltonian

We consider an isolated molecule formed by N particles (nuclei and electrons) with masses $\{M_i\}$ and charges $\{Q_i\}$. The positions of the particles are first described in a laboratory Cartesian coordinate system. The laboratory coordinates and the corresponding linear momenta of the particles are:

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

The nonrelativistic laboratory-frame Hamiltonian of the system is:

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

Next, the $3N$-dimensional problem represented by the above Hamiltonian is separated into two problems. The first is 3-dimensional problem of the motion of the center of mass of the molecule is space. The second is an $(3N-3)$-dimensional internal problem of the motions of the particles forming the molecule with respect to each other. This separation is rigorous and is 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 Cartesian coordinates. These coordinates denoted as $\mathbf{r}_i$, $i = 1, ..., N-1$, are position vectors of particles 2 to N with respect to particle 1 called the reference particles (usually the heaviest nucleus in the molecule). Let $n = N-1$. In the new coordinate system Hamiltonian (2) is:

$$H_{\mathrm{nr}}^{\mathrm{tot}}\left(\mathbf{r}_0, \mathbf{r}\right) = \left(-\frac{1}{2}\frac{1}{M_{\mathrm{tot}}}\nabla_{\mathbf{r}_0}^2\right) + \left(-\frac{1}{2}\sum_{i}^{n}\frac{1}{\mu_i}\nabla_{\mathbf{r}_i}^2 - \frac{1}{2}\sum_{i\neq j}^{n}\frac{1}{m_0}\nabla_{\mathbf{r}_i}^T\nabla_{\mathbf{r}_j} + \sum_{i<j}^{n}\frac{q_i q_j}{r_{ij}} + \sum_{i=1}^{n}\frac{q_0 q_i}{r_i}\right), \tag{3}$$

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 $r_{0i} \equiv r_i = \|\mathbf{r}_i\| = \|\mathbf{R}_{i+1} - \mathbf{R}_1\|$.

As one can see, in the new coordinate system, lab-frame Hamiltonian (3) becomes a sum of operators representing the kinetic energy of the center-of-mass motion, $H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0)$, and the internal Hamiltonian, $H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r})$:

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

where the three components of vector $\mathbf{r}$ are the coordinates of $\mathbf{r}_1$, the next three are coordinates of $\mathbf{r}_2$, etc. 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. It involves diagonalization of the matrix of the internal Hamiltonian and the overlap matrix. The computational time for calculating a matrix element of each of the two matrices is, in general, proportional to the product of the factorials of the numbers of particles in the groups of identical particels. This dependency results from the number of symmetry operators that need to be applied to the wave function to impose the proper permutational symmetry.

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 $(i = 1, ..., n)$ 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 the introduction, the internal Hamiltonian, (3), has the symmetry of an atomic Hamiltonian.

3. Basis functions

In selecting the basis functions for expanding the spatial parts of the eigenfunctions of the internal Hamiltonian the following needs to be taken into consideration:

1. If nuclei and electrons in the calculation are treated on equal footing, the nucleus-nucleus (n-n), electron-electron (e-e), and nucleus-electron (n-e) correlation need to be represented in the wave function. The most effective form of this representation involves expanding the wave functions in terms of basis functions which explicitly depend on the inter-particle distances. Such functions are usually called explicitly correlated functions. There has been various types of explicitly correlated functions used in quantum mechanical (QM) calculations of electronic structures of small molecules based on the BO approximation, however similar calculations where the BO approximation is not assumed is a more recent development in the field of molecular quantum mechanics. Such calculations require different basis functions as the effects that need to be described in the calculations are more intricate than in the calculations concerning electronic states. The e-e, n-e, and n-n correlation effects are due to the electrostatic interactions between the particles, but they are also dependent on particles' masses. As electrons are light and have unit negative charges the inter-electron correlation is relatively weak. This is manifested by their wave functions overlapping to some degree resulting in non-negligible probability of finding two electrons (with opposite spins) at the same point is space. On the other hand, due to significantly larger masses of the nuclei, the inter-nuclear correlation is stronger because the nuclei "avoid" each other to much higher degree in their motion inside the molecule than the much lighter electrons. The third type of correlation, the n-e correlations, can be called anti-correlation, as it describes an effect of electrons, particularly the core electrons, following the nuclei very closely. The dependence of the basis functions on the electron-nucleus distances helps to accurately describe these effects.
2. We have used varies forms of explicitly correlated one-center Gaussian functions (ECGs) in our molecular non-BO calculations. The key component of these functions, the Gaussian exponent, can be represented, e.g. for an atom with s electrons, in the following form, which shows its explicit dependence on the inter-particle distances, r_{ij}:

$$\phi_k = \exp[-\alpha_{1k} r_1^2 - \alpha_{2k} r_2^2 - \ldots - \alpha_{nk} r_n^2 - \beta_{12,k} r_{12}^2 - \beta_{13,k} r_{13}^2 - \ldots - \beta_{nn-1,k} r_{nn-1}^2], \quad (5)$$

where n denotes the number of particles, r_i is the distance between particle i and the center of the Gaussian, and α_{ik} and $\beta_{ij,k}$ and the non-linear parameters of the k Gaussian, which can be optimized using the variational method. The above functions can be represented using the following alternative shorter form as:

$$\phi_k(\mathbf{r}) = \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}], \quad (6)$$

where $\bar{\mathbf{A}}_k$ is a $3n \times 3n$ real symmetric matrix of exponential parameters. $\bar{\mathbf{A}}_k$ can be written as: $\bar{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$, where $\mathbf{I}_3$ is the 3×3 unit matrix, $\otimes$ denotes the Kronecker product, and $\mathbf{A}_k$ is a $n \times n$ symmetric matrix. To ensure square integrability of $\phi_k(\mathbf{r})$, matrix $\mathbf{A}_k$ must be positive definite. This is automatically achieved if $\mathbf{A}_k$ 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.

3. While the e-e correlation can be quite adequately described by ECGs only dependent on the e-e distances in the Gaussian exponent, the stronger n-n correlation, as we have demonstrated with the non-BO calculations of bound states of some small diatomic molecules [4–6], requires pre-exponential multipliers in the form of non-negative powers of the inter-nuclear distance (the intermolecular distances for molecules with more than two nuclei). The presence of these terms in the ECGs is also important in representing vibrationally excited states, which have nodes in terms of the inter-nuclear coordinates. We call ECGs with such multipliers "power Gaussians" in this work. For a diatomic system a power Gaussian has the following form:

$$\phi_k(\mathbf{r}) = r_1^{2m_k} \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}], \quad (7)$$

where one of the nucleus is selected to be the reference particle, particle 2 is the second nucleus. Thus, r_1 is the inter-nuclear distance and $2m_k$ is its power. The power is an even non-negative number. As we demonstrated, limiting the powers to be even numbers does not affect the accuracy of the calculation, but simplifies the algorithms for calculating the Hamiltonian matrix elements. The larger the $2m_k$ power the more the nuclei are separated from each other. Zero value of the power needs to be included to assure that the probability of finding the nuclei in a single point in space may not be exactly zero. In non-BO calculations of molecules with more than two nuclei, the pre-exponential multiplier, $r_1^{2m_k}$, needs to be extended to include powers of all inter-nuclear distances. Thus, for a triatomic, the multiplier is $r_1^{2m_k} r_2^{2n_k} r_{12}^{2l_k}$, where the third nucleus in particle 3. We made an attempt to implement ECGs with such multipliers in non-BO calculations, but it was unsuccessful due to oscillatory nature of the algorithms for calculating the Hamiltonian matrix elements resulting in numerical inaccuracies which could not be controlled [7].

4. In recent years we have developed and tested an alternative form of ECGs for molecular non-BO calculations [8,9]. These alternative basis functions are explicitly correlated Gaussians with complex exponential parameters (complex ECGs (CECGs)). The general form of such functions is:

$$\phi_k(\mathbf{r}) = \exp[-\mathbf{r}^T \bar{\mathbf{C}}_k \mathbf{r}] = \exp[-\mathbf{r}^T (\bar{\mathbf{A}}_k + \mathrm{i}\bar{\mathbf{B}}_k) \mathbf{r}], \quad (8)$$

where $\bar{\mathbf{A}}_k$, as in (6), 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: $\bar{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$ and $\bar{\mathbf{B}}_k = \mathbf{B}_k \otimes \mathbf{I}_3$.

To ensure square integrability of $\phi_k(\mathbf{r})$, matrix $\mathbf{A}_k$, as in (6), is represented in the Cholesky factored form as: $\mathbf{A}_k = \mathbf{L}_k \mathbf{L}_k^T$. The $\mathbf{L}_k$ matrix elements can be any real numbers. We demonstrated in our recent works that functions (8) can be contracted to form pre-exponential multipliers being products of *sin* and *cos* functions dependent on squares of the inter-particles distances [10]. Such products can very effectively represent the e-e, n-n, and n-e correlation effects. They can also describe the oscillations and nodes of the wave functions in rovibrational excited states as effectively as the power Gaussians and, what is even more important, such basis functions can potentially be universal, i.e., can be used in the non-BO calculations of molecules with two or more nuclei.

5. The internal Hamiltonian in the non-BO approach commutes with the operator representing the square of the total angular momentum and with operator representing its z-coordinate. Thus, if the basis functions used in the calculation are eigenfunctions of these two operators, the Hamiltonian and overlap matrices are block-diagonal. In our previous works we implemented algorithms for calculating excited rovibrational states of diatomic systems corresponding to the total angular-momentum quantum numbers of one and two using the power ECGs [13–15]. The angular factors of the Gaussians were Cartesian spherical harmonics. The implementation of the former case was first carried out using the following basis functions:

$$\phi_k(\mathbf{r}) = z_1 r_1^{2m_k} \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}], \quad (9)$$

where z_1 is the z coordinate of the $\mathbf{r}_1$ vector. m_k is a non-negative integer. Such a basis restricts the angular (rotational) excitation to the nuclei. More recently we removed this restriction and implemented the ECG basis set with z_1 replaced by z_i:

$$\phi_k(\mathbf{r}) = z_i r_1^{2m_k} \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}], \quad (10)$$

where index i spans the range $1, \ldots, n$. Such a basis set allows the angular excitation of the molecule to be a superposition of nuclear rotational excitation and electron angles excitations. The generalization of the ECG basis resulted in a noticeable improvement of the results. However, the replacement of the $z_1 r_1^{2m_k}$ pre-exponential factor by the $z_i r_1^{2m_k}$ factor resulted in more complex algorithms for calculating the Hamiltonian matrix elements. Also, a generalization of basis (9) to calculate higher angular-momentum states would lead to even more complicated algorithms.

6. Considering the above, effort is now beening devoted to the implementation of the CECG basis sets with pre-exponential factors being Cartesian spherical harmonics for calculating ground and excited rovibrational states of diatomics, as well as of molecules with more than two nuclei. In the present work we implement and test algorithms for performing non-BO molecular calculations of rovibrational states corresponding to the total angular-momentum quantum number of one. The following CECGs are used:

$$\phi_k(\mathbf{r}) = z_i \exp[-\mathbf{r}^T (\bar{\mathbf{A}}_k + \mathrm{i}\bar{\mathbf{B}}_k) \mathbf{r}]. \quad (11)$$

Functions (11) are simpler than functions (10) with the z_i angular factor because the $r_1^{2m_k}$ is absent. This makes the evaluation of the Hamiltonian matrix elements simpler, as was shown in our previous work [11].

4. Computational implementation

The algorithms for the Hamiltonian and overlap matrix elements for CECGs (11) derived in our previous work [11] are implemented on a parallel computer platform using Frotran90 and MPI (message passing interface). The implementation also includes the matrix elements of the analytical energy gradient determined with respect to the matrix elements of $\mathbf{L}_k$ and $\mathbf{B}_k$, i.e. the Gaussian non-linear parameters. The implementation is general and can be applied to an arbitrary number and types of particles. The procedures for calculating the matrix elements are called by the optimization routine that minimizes the total non-relativistic internal energy of a particular state of the considered system. The routine calculates the energy by constructing the Hamiltonian and overlap matrices and by solving the secular equation. It also uses the energy gradient to navigate the search for the energy minimum in terms of the $\mathbf{L}_k$ and $\mathbf{B}_k$ parameters. The basis set is generated separately for each state in a process that involves adding basis

Table 1
Comparison of the total energies of all (v;1) rovibrational states, i.e. vibrational states corresponding to the total rotational quantum number of one, of HD^+ with the number of ECG and CECG basis functions. [a]Calculations performed with the ECGs containing the z_1 angular factors; Eq. (9) (the results are taken from Ref. [13]); [b]calculations performed with ECGs containing the z_i angular factors; Eq. (10) (the results are taken from Ref. [14]); [c]present results. Energy is given in hartrees.

v	No. of ECGs[a]	Energy	No. of ECGs[b]	Energy	No. of CECGs[c]	Energy
0	1000	−0.597698117270			1300	−0.597698126833
	2000	−0.597698117430	2000	−0.597698128157	1400	−0.597698127708
1	1000	−0.588991101048			1300	−0.588991109211
	2000	−0.588991101393	2000	−0.588991111891	1400	−0.588991111051
2	2000	−0.580721817887			1300	−0.580721821645
	3000	−0.580721817949	3000	−0.580721828098	1400	−0.580721825717
3	2000	−0.572877266933			1300	−0.572877264452
	3000	−0.572877267102	3000	−0.572877276952	1400	−0.572877272234
4	2000	−0.565446156398			1300	−0.565446140543
	3000	−0.565446156586	3000	−0.565446166143	1400	−0.565446155218
5	2000	−0.558418853179			1300	−0.558418816117
	3000	−0.558418853772	3000	−0.558418863010	1400	−0.558418841953
6	3000	−0.551787358384			1300	−0.551784813885
	4000	−0.551787358546	4000	−0.551787367661	1400	−0.551785362736
7	3000	−0.545545294252			1300	−0.545545176971
	4000	−0.545545294365	4000	−0.545545303218	1400	−0.545545246885
8	3000	−0.539687917327			1300	−0.539687805034
	4000	−0.539687917664	4000	−0.539687926437	1400	−0.539687858051
9	3000	−0.534212153253			1300	−0.534211960249
	4000	−0.534212153571	4000	−0.534212161742	1400	−0.534212052045
10	3000	−0.529116643823			1300	−0.529116392004
	4000	−0.529116644298	4000	−0.529116652126	1400	−0.529116530299
11	3000	−0.524401837382			1300	−0.524401445152
	4000	−0.524401837887	4000	−0.524401845428	1400	−0.524401679662
12	3000	−0.520070088900			1300	−0.520069637976
	4000	−0.520070089352	4000	−0.520070097632	1400	−0.520069890179
13	3000	−0.516125824708			1300	−0.516125031933
	4000	−0.516125825569	4000	−0.516125832377	1400	−0.516125471367
15	4000	−0.509428840269			1300	−0.509427927964
	5000	−0.509428841143	7000	−0.509428847836	1400	−0.509428413768
16	5000	−0.506697146745			1300	−0.506695635863
	6000	−0.506697147635	7000	−0.506697153549	1400	−0.506696459296
17	5000	−0.504395560512			1300	−0.504393797468
	6000	−0.504395562033	7000	−0.504395568117	1400	−0.506696459296
18	5000	−0.502542374245			1300	−0.502540442229
	6000	−0.502542376164	7000	−0.502542383121	1400	−0.502541521177
19	6000	−0.501159138174			1300	−0.501157061986
	7000	−0.501159139178	8000	−0.501159145991	1400	−0.501158220861
20	6000	−0.500269319648			1300	−0.500267274996
	7000	−0.500269319879	7000	−0.500269322550	1400	−0.500268029383
21	6000	−0.499902780157			1300	−0.499902253252
	7000	−0.499902780540	7000	−0.499902781600	1400	−0.499902454450
22	6000	−0.499864341698			1300	−0.499864243170
	7000	−0.499864342032	7000	−0.499864342146	1400	−0.499864244585

functions one by one. The initial guess for an added function is obtained by applying random perturbation to the non-linear parameters of a subset of some most contributing functions already included in the basis set and selecting the function that after perturbation lowers the energy the most. For that function the i index in pre-exponential multiplier z_i is optimized first and this is followed by the optimization of the function's $\mathbf{L}_k$ and $\mathbf{B}_k$ parameters. At this point the overlap integrals between the optimized functions and the functions already included in the basis set are calculated to check for linear dependencies. If any are found the function is discarded and a new function is selected and optimized. After addition of a certain number of new functions the whole basis set is reoptimized by cycling over all functions one by one and re-optimizing their $\mathbf{L}_k$ and $\mathbf{B}_k$ parameters (no reoptimization of the i index is done at this point). The growing of the basis set continues until the desired energy convergence is reached.

The computational costs for calculating the matrix elements with CECGs and with the power ECGs are similar. However, solving of the secular equation for CECGs takes somewhat more time than the for power ECGs, as it involves diagonalization of complex Hamiltonian and overlap matrices. The test calculations are performed for all 23 bound rovibrational states of the HD^+ ion with the total-angular-momentum quantum number of one (the (v = 0, ...,22; 1) states). Basis set (11) is used in the calculations. HD^+ is chosen as test case for the present calculations because its (v; 1) states were calculated before both with the basis functions (9) and (10) [12–14].

One question which may arise regarding the choice of the basis functions used in the present calculations is why we choose to use complex Gaussians (11) and not their real *sin*/*cos* linear combinations formed as described in Ref. [10]. As the wave functions for the (v = 0, ...,22; 1) states are real, one may think that the use of real basis set would be better than using complex basis functions (11). However, by allowing the variational optimization of CECGs (11) to be carried out without any constrains, thus allowing the wave function to extend to the complex plain, may open additional optimization trajectories in the space of the non-linear parameters that lead to faster convergence of the calculation to the final solution which is the real wave function and the corresponding real energy value. However, at the end of the variational optimization the resulting wave function may still contain some residual "imaginary" contamination. This does not present a problem as the result is still strictly variational.

In the first step, the basis sets containing 1300 CECGs previously generated for the (v = 0, ...,22, 0) states of HD^+ are used to generate the initial guesses for the basis sets for calculating the (v = 0, ...,22; 1) states. At first each (v = 0, ...,22, 0) basis function is multiplied by z_1.

Table 2
Comparison of the total energies of the three lowest (v;1) rovibrational states, i.e. vibrational states corresponding to the total rotational quantum number of one, of HD^+ with the number of ECGs (with the z_i angular factors) and CECGs. The ECG results are taken from Ref. [14]). They were obtained with basis functions (10). Energy is given in hartrees.

v	No. of CECGs	No. of ECGs	Energy
0	1300		−0.597698126833
	1400		−0.597698127708
	1500		−0.597698127904
	1600		−0.597698127982
	1700		−0.597698128020
		2000	−0.597698128157
1	1300		−0.588991109211
	1400		−0.588991111051
	1500		−0.588991111425
	1600		−0.588991111588
	1700		−0.588991111649
	2000	2000	−0.588991111891
2	1300		−0.580721821645
	1400		−0.580721825717
	1500		−0.580721826629
	1600		−0.580721827017
	1700		−0.580721827195
		3000	−0.580721828098

Next a variational calculation is performed for each state where the index of the z_1 multiplier for each basis function is optimized to either remain equal to 1 or is changed to 2. This is the only point in the procedure where index i of the z_i pre-exponential angular multiplier is optimized. Next the 1300-CECG basis set for each state is fully optimized, i.e. the $\mathbf{L}_k$ and $\mathbf{B}_k$ parameters for each basis functions are variationally optimized using the variational procedure that employs the analytical energy gradient. This optimization is followed for each state with a calculation where the basis set of that state is grown from the size of 1300 to the size of 1400. In the next step each 1400-CECG basis set is extensively optimized. The total non-BO energies obtained in the calculations performed with 1300 and 1400 CECGs are shown in Table 1. These energies are compared with our best results obtained for the ($v = 0, ..., 22$; 1) states with basis functions (9) and (10). The purpose of the comparison is to test the correctness of the procedure implemented in this work.

Upon examining the results in Table 1 one notices that the CECG energies in general agree with the ECG results. However, as the ECG results were obtained with the number of functions that increased from 2000 for the lowest energy state to 7000–8000 for the highest energy states, the energy gap between the CECG and ECG energies increases with the vibrational excitation. For the $v = 0$ state, the CECG energy is lower than the energy obtained with ECGs with the z_1 but it is slightly higher than the energy obtained with ECGs with and z_i angular multipliers. The some also happens for states $v = 1$, 2, 3, and 4. As the level of the vibrational excitation increases and the number of the CECGs stays at the constant level of 1400 functions, while the number of ECGs increases to 7000–8000 functions, the CECG energies become progressively worse. It is clear that more CECGs is needed to match the ECG results.

In the last series of the calculations the number of CECGs is graduately increased from 1400 to 1700 for the lowest three vibrational states to check if CECGs are capable to deliver comparable accuracy as reached with ECGs that contain the z_i angular pre-exponential multipliers. The results are shown in Table 2. As one can see, the CECG energies for all three states converge within 10^{-9} hartree to the ECG results.

Based on the above results we can conclude that the implementation of the algorithm for calculating the (v;1) rovibrational states is correct. Some more applications of the procedure are forthcoming.

5. Summary

The explicitly correlated complex all-particle Gaussian functions are very promising basis functions to extend the applicability of the non-BO approach to calculate rovibrational spectra of molecules with more than two nuclei. In this work we implement a procedure for calculating rovibrational states corresponding to the rotational quantum number of one. The implementation is general and can be used in calculations of molecular systems (or, in general, clusters of particles) with an arbitrary number of particles of any types. The implemented procedure is tested in the calculations of the (v;1) spectrum of the HD^+ ion. The test validates the correctness of the implementation. Our next project is to perform non-BO calculations of rovibrational spectra of H_3^+ and its isotopologues using CECGs. Some of the H_3^+ spectral lines will be calculated with the procedure implemented in the present work.

Conflict of interest

The authors declared that there is no conflict of interest.

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