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Universal all-particle explicitly-correlated Gaussians for non-Born–Oppenheimer calculations of molecular rotationless states

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ABSTRACT

Complex explicitly correlated one-center all-particle Gaussian functions (CECGs) are tested as basis functions for molecular non-Born–Oppenheimer (non-BO) calculations. The tests concern the complete spectrum of the 23 bound pure vibrational states of the HD⁺ ion. The tests show that CECGs are very effective in representing both the nuclear-nuclear correlation and the vibrational oscillation of the wave functions in terms of the internuclear distance. This finding is important because it paves the way for high-accuracy non-BO calculations of bound vibrational states of molecules with more than two nuclei that have never been performed before.

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Accurate quantum-mechanical calculations of bound states of molecular systems without assuming the Born-Oppenheimer (BO) approximation provide a unique way of describing the properties of these systems without any approximations concerning the separability of the motions of the nuclei and electrons. They are also capable of producing very accurate results concerning the spectral transitions in these systems. Non-BO molecular calculations require the use of unconventional basis sets different from the basis sets used the BO calculations, because the motion of all particles in the system, i.e. nuclei and electrons, are treated on equal footing. As one of the main goals to carry out non-BO calculations is to achieve very high accuracy, the basis functions used to expand the wave function have to be explicitly dependent on the inter-particle (i.e. electron-electron, electron-nucleus, and nucleus-nucleus) distances. In our atomic and molecular non-BO calculations, the explicitly correlated Gaussians (ECGs) have been such functions [1,2].

High-accuracy calculations of the rovibrational spectra of small molecular systems have been of interest to the quantum chemists from the very beginning. In recent years such calculations have involved several different approaches such as, for example, the artificial-channels method of Balint-Kurti et al. [3] and Moss [4],

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http://dx.doi.org/10.1016/j.cplett.2016.01.056 0009-2614/© 2016 Elsevier B.V. All rights reserved. the Lagrange-mesh method of Pilon and Baye [5], and various other methods specifically designed to study three-particle systems [6–8]. In some of these methods the Born–Oppenheimer (BO) approximation was not assumed from the start. Other methods assumed the BO approximation and employed the electronic BO potential energy surface augmented with adiabatic, nonadiabatic, relativistic, and radiative corrections as the potential in the Schrödinger equation representing the motion of the nuclei, which was solved to determine the rovibrational energies [9,10].

A feature that differentiates the non-BO calculations from the electronic BO calculations are different masses and charges of the considered particles. A considerable experience has been gained through the electronic structure calculations concerning the phenomenon called the electron-electron correlation. This correlation can be separated into the dynamic and non-dynamic 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 because either the system is electronically excited or a chemical bond between two atoms is dissociating. If this bond is a single bond, one electron forming the bond stays by one atom and the other electron moves away with the other atom. If nuclei in the calculations are treated on equal footing with the electrons, a nucleus-nucleus correlation, as well as nucleus-electron correlation, appear and have to be represented in the wave function. The nature of the nucleus-nucleus correlation is different than the electron-electron correlation, even though both correlations result from the Coulombic repulsion. The reason for the difference is the significantly different masses of the two types of particles which makes the wave

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functions of the lighter electrons to much more significantly overlap than the wave functions of the heavier nuclei. In effect the nuclei avoid each other to much greater extent than the electrons.

We have demonstrated with the non-BO calculations of bound states of some small diatomic molecules [2] that an accurate description of the nucleus-nucleus correlation requires addition to the exponentially correlated all-particle single-center Gaussians pre-exponential multipliers in the form of non-negative powers of the internuclear distance (we call them 'power Gaussians'). The larger is 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 powers also allow for describing nodes in the wave function which appear when the molecule is excited to higher vibrational states. An important property of the ECGs with the pre-exponential powers of the internuclear distance is their spherical symmetry with respect to the center of the coordinate system. As the Hamiltonian used in our molecular non-BO calculations is also spherically symmetric (i.e. isotropic), its eigenfunctions are 'atom-like' and transform according to the irreducible representations of the SO(3) rotation group. In particular, the wave functions representing the rovibrational states corresponding to the lowest value of the rotational quantum number (N=0; the rotational ground state), which are the subject to the calculations presented in this work, are fully symmetric with respect to the center of the coordinate system. For expanding such wave functions fully symmetric basis functions, such as power Gaussians, have to be used.

The pre-exponential multipliers in the power Gaussians do not need to include terms dependent on the inter-electron distances as the electron correlation is quite adequately described by the Gaussian exponent being dependent on these distances. The power terms in the pre-exponential multipliers also do not need to include powers of the nucleus-electron distances. As the ECGs have maxima at the zero electron-nuclei distances, they can very effectively describe the correlated motions of the nuclei and the electrons.

Extending the use of power Gaussians to describe rovibrational states of molecules with three nuclei requires that the pre-exponential multipliers include powers of all three internuclear distances. This would enable an accurate description of both the highly correlated motion of the nuclei and the oscillation of the wave function corresponding to vibrational excitations. A while ago we derived expressions for the the Hamiltonian and overlap integrals for such Gaussians [11], but an attempt to implement them on a computer failed due to the oscillatory nature of these algorithms that caused numerical instabilities in the calculation.

The (non-relativistic) Hamiltonian used in our non-BO calculations is obtained by separating out the center of-mass motion from the full nonrelativistic laboratory-frame Hamiltonian of the system. It involves all particles forming the system being treated on equal footing. The separation starts with the laboratory-frame Hamiltonian expressed in terms of laboratory Cartesian coordinates. Denoting the total number of particles (i.e. the electrons and the nuclei) as n+1 and their masses, charges, and positions as M_i , Q_i , and \mathbf{R}_i , respectively, where i = 1, ..., n+1, the laboratory-frame nonrelativistic Hamiltonian, \hat{H}_{lab} , that includes the kinetic energy operators of all particles and the Coulombic interactions within each pair of particles is:

$$\hat{H}_{lab} = -\sum_{i=1}^{n+1} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^{n+1} \sum_{j>i}^{n+1} \frac{Q_i Q_j}{R_{ij}},\tag{1}$$

where $R_{ij} = |\mathbf{R}_j - \mathbf{R}_j|$ are the interparticle distances. The separation of the center-of-mass motion from \hat{H}_{lab} is accomplished by a transformation to a new Cartesian coordinate system, whose first three coordinates are the coordinates of the center of mass in the

laboratory coordinate system, and the remaining 3n coordinates are coordinates describing the internal motion of the system. The internal coordinates are defined with respect to a selected particle (usually the heaviest one; it is called the reference particle and numbered as particle 1) where the origin of the internal coordinate system is placed. The internal coordinates are defined as $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$. After transforming \hat{H}_{lab} to the new coordinate system, it rigorously separates into the kinetic energy operator of the center-of-mass motion and a Hamiltonian, \hat{H} , dependent only on the \mathbf{r}_i coordinates which represents the internal motion of the system. The internal Hamiltonian is:

$$\hat{H} = -\frac{1}{2} \left(\sum_{i}^{n} \frac{1}{\mu_{i}} \nabla_{i}^{2} + \sum_{i \neq j}^{n} \frac{1}{M_{1}} \nabla_{i}^{\prime} \nabla_{j} \right) + \sum_{i=1}^{n} \frac{q_{0}q_{i}}{r_{i}} + \sum_{i \neq j}^{n} \frac{q_{i}q_{j}}{r_{ij}}.$$
 (2)

 \hat{H} describes a system of *n* particles (pseudoparticles) with charges $q_i = Q_{i+1}$ and masses $\mu_i = M_1 M_{i+1}/(M_1 + M_{i+1})$ moving in the central field of the charge of the reference particle. The masses of the proton and deuteron used in the present calculations are: $M_p = 1836.15267261$ and $M_d = 3670.4829652$ [12]. r_i and r_{ij} in (2) are defined as $r_i = |\mathbf{R}_i - \mathbf{R}_1| = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{R}_j - \mathbf{R}_i| = |\mathbf{r}_j - \mathbf{r}_i|$. Prime (') denotes the vector/matrix transposition. The spherical symmetry (isotropy) of the internal Hamiltonian is evident.

Defining the **r** as a $3n \times 1$ vector of the internal Cartesian coordinates, **r**_{*i*}, of the *n* pseudoparticles (**r**' = (**r**'₁, **r**'₂, ..., **r**'_n)), the power Gaussian has the following form [13,14]:

$$\phi_k = r_1^{2m_k} \exp[-\mathbf{r}'(\mathbf{A}_k \otimes \mathbf{I}_3)\mathbf{r}],\tag{3}$$

where \mathbf{A}_k is a positive-definite symmetric matrix of exponential coefficients and \mathbf{I}_3 is the 3 × 3 identity matrix. The pre-exponential multiplier in (3) is the internuclear distance, r_1 , raised to a non-negative even power $2m_k$. m_k varies from 0 to 125 in our non-BO calculations. The ϕ_k functions (called ECGs in this work) have provided a very effective set of functions for expanding the non-BO wave functions of the N = 0 rovibrational states of diatomic systems.

In our non-BO calculations we use the standard variational method which facilitates a way for the optimization of the Gaussian non-linear parameters. This optimization is performed with the aid of the analytical energy gradient determined with respect to these parameters [1,2]. The use of the gradient is key to obtain very accurate results in the calculations.

There is another type of explicitly correlated functions which we introduced to perform non-BO atomic and molecular calculations [15]. They are all-particles one-center correlated Gaussians, which only depend on the interparticle distances is the Gaussian exponent, but their exponential parameters are complex numbers:

$$\phi_k = \exp[-\mathbf{r}'((\mathbf{A}_k + \mathbf{i}\mathbf{B}_k) \otimes \mathbf{I}_3)\mathbf{r}],\tag{4}$$

where $i = \sqrt{-1}$ and **B**_k is a real symmetric matrix. Unlike in ECGs (3), all particles in complex ECGs (4) (CECGs) are treated equivalently and no distinction is made between the nuclei, which in (3)are described by additional pre-exponential factors, and the electrons, which are only described through the dependence of (3) in the Gaussian exponent on the electronic coordinates. In the work where functions (4) were introduced we also presented formulas for calculating the Hamiltonian and overlap matrix elements with these functions for the general *n*-particle case, as well as the matrix elements of the analytical gradient determined with respect to the \mathbf{A}_k and \mathbf{B}_k matrix elements. Even though some test calculations were performed for some lower lying states of a diatomic system, we concluded that functions (4) are probably less effective in diatomic non-BO calculations than functions (3). In the present work we present an evidence that contradicts this initial assessment. A series of calculations using functions (4) are performed for all 23 bound rotationless (i.e. N=0) states of the HD⁺

Table 1

A comparison of the total non-BO energies of all 23 bound rovibrational states ($\nu = 0, ..., 22$) of the HD⁺ ion corresponding to the zero total rotational quantum number (N=0) obtained with the ECGs of Eq. (3) and CECGs of Eq. (4). The number of Gaussians in the basis set used is shown for both basis sets. Energies are in hartrees.

ν	No. of Gaussians	Energy	ν	No. of Gaussians	Energy	ν	No. of Gaussians	Energy
0	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5978979676 -0.5978979683 -0.5978979684 -0.5978979686	8	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5398197233 -0.5398203866 -0.5398205652 -0.5398206406	16	600 CECG 800 CECG 1000 CECG 6000 ECG	-0.5067526133 -0.5067603668 -0.5067628218 -0.5067638738
1	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5891818255 -0.5891818284 -0.5891818292 -0.5891818295	9	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5343354614 -0.5343366096 -0.5343369013 -0.5343370131	17	600 CECG 800 CECG 1000 CECG 6000 ECG	-0.5044393111 -0.5044484939 -0.5044514710 -0.5044526917
2	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5809036874 -0.5809036966 -0.5809036992 -0.5809037002	10	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5292315326 -0.5292330268 -0.5292334637 -0.5292336347	18	600 CECG 600 CECG 1000 CECG 6000 ECG	-0.5025755337 -0.5025845953 -0.5025877988 -0.5025892273
3	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5730505116 -0.5730505373 -0.5730505439 -0.5730505465	11	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5245078210 -0.5245101263 -0.5245106768 -0.5245109096	19	600 CECG 800 CECG 1000 CECG 7000 ECG	-0.5011808246 -0.5011906237 -0.5011933855 -0.5011947942
4	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5656109463 -0.5656110165 -0.5656110348 -0.5656110420	12	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5201668138 -0.5201699766 -0.5201707987 -0.5201711438	20	600 CECG 800 CECG 1000 CECG 7000 ECG	-0.5002794588 -0.5002885302 -0.5002910444 -0.5002924536
5	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5585753319 -0.5585754716 -0.5585755074 -0.5585755207	13	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5162130075 -0.5162169958 -0.5162182380 -0.5162187089	21	600 CECG 800 CECG 1000 CECG 7000 ECG	-0.4999049760 -0.4999088481 -0.4999098597 -0.4999103595
6	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5519355865 -0.5519358508 -0.5519359231 -0.5519359486	14	600 CECG 800 CECG 1000 CECG 5000 ECG	-0.5126530755 -0.5126578245 -0.5126595518 -0.5126601913	22	600 CECG 800 CECG 1000 CECG 7000 ECG	-0.4998538944 -0.4998651297 -0.4998656097 -0.4998657783
7	600 CECG 800 CECG 1000 CECG 4000 ECG	-0.5456853090 -0.5456857566 -0.5456858717 -0.5456859150	15	600 CECG 800 CECG 1000 CECG 5000 ECG	-0.5094953721 -0.5095018290 -0.5095038244 -0.5095046474	p + D		-0.4998638152

ion. The results are compared with the results obtained previously using functions (3) [16].

We will now describe some details of the calculations performed in this work to test the ability of CECGs (4) to represent bound pure vibrational non-BO molecular states. The most difficult features in such states that the CECGs need to describe is the almost zero probability of finding two nuclei in a single point in space and the vibrational oscillation of the wave function in terms of the internuclear distance (r_1). As mentioned, these features are very effective described by ECGs (3) due to their including the $r_1^{2m_k}$ factors.

The problem of determining the energies of the pure vibrational states of HD⁺ is a three-particle problem in the non-BO calculations. In the calculations each of the 23 states is treated separately from other states and the CECG basis set is generated separately for each state. In the first step the ground state ($\nu = 0$) is considered and the calculation of its CECG basis set starts with only ten randomly chosen functions. The non-linear parameters of these functions (i.e. the \mathbf{A}_k and \mathbf{B}_k matrix elements) are fully variationally optimized using the approach employing the analytical energy gradient [15]. In the next step the basis set is grown by adding one CECG at a time to reach the size of 300 functions. The initial form of each new function is obtained for a random perturbation applied to some most contributing functions already included in the basis set and choosing the one which lowers the total energy the most. After the function is optimized it is checked for linear dependencies with the existing functions and, if any is found, the function is discarded and a new function is chosen and optimized. After the addition of each 20 functions, the whole basis set is reoptimized again using the one-function-at-a-time approach. Once the

300-CECG basis set is generated for the ground state, it is used as the initial guess in the calculation of the first excited state ($\nu = 1$). While this basis is being optimized, the growing of the basis set for the ground state continues. After the 300-CECG basis is optimized for the first excited states it is used as the initial guess for the basis set for the second excited state (ν =2). The process continues until 1000-CECG basis sets for all 23 states are generated. For the highest 23-rd state (ν = 22) the initial basis set is the 600-CECG basis set taken from the 22-nd state (ν = 21). In generating the basis set for the v = 1, ..., 21 states the size of the initial basis set is gradually increased from 300 to 600. The results showing the convergence of the total non-BO CECG energies for all 23 states are shown in Table 1. The results are compared with the best energies obtained for the states using ECGs (3). The differences between the CECG energies and the ECG energies are plotted in Figure 1.

As the results shown in Table 1 indicate the energy convergence obtained at the level of 1000 CECGs in comparison with the very accurate ECG calculations is very good considering that the ECG basis sets include many more functions (the number of the ECGs varies from 4000 to 7000). For the ground and the first excited state the difference between the best CECG and ECG energies is in the 10-th significant figure. The differences gradually increase to be in the 9-th significant figure for the v=2-7 states, in the 8-th significant figure for the v=5-8 states, in the 7-th significant figure for the v=9-16 states, and in the 6-th significant figure for the v=17-20 states. For the top two states (v=21 and v=22) the difference again drops to be in the 7-th significant digit. Naturally, in order to reduce the differences one needs to add



Figure 1. Difference in total non-BO energies obtained for 23 bound pure vibrational states of HD⁺ with power Gaussians and complex Gaussians. Logarithmic scale is used. The results are in hartrees.

more CECGs to the basis sets. Increasing the CECG basis set sizes should be done unevenly with more functions added to the higher states. However, it is interesting that for the top states, despite still using 1000 CECGs in calculating them, the differences between the corresponding ECG and CECG energies decrease. This can be explained by the different characers of the ECGs and CECGs with the former having only one maximum in terms of the r_1 coordinate and the latter oscillating in terms of this coordinate (this oscillation can be better seen if CECGs are combined to form Gaussians with real sin/cos pre-exponential multipliers). As the wave functions for the higher vibrational states also become more oscillatory, the CECGs may be better basis functions for expanding them than ECGs.

The addition of more CECGs to the basis sets is currently limited by the computer time taken by solving the secular equation involving complex Hamiltonian and overlap matrices in each iteration step of the optimization of the CECG non-linear parameters. A procedure for a fast complex-matrix diagonalization is being developed and will be used in future molecular applications of the CECG approach. In mean time, however, in order to perform an additional test of the performance of CECGs, an effort is made involving increasing the basis set for several lowest HD⁺ pure vibrational states to 1300 functions. Then the energies obtained in the calculations are compared with the energies obtained with the ECG basis set with different sizes to see how many ECGs it takes to obtain a similar energy as using 1300 CECGs. A comparison between the two sets of energies for the lowest eight vibrational states is shown in Table 2. As one can see, for the ground state the 1300-CECG result reproduces the ECG energy obtained with 4000 Gaussians. The same happens for the first excited state. For the higher states the 1300-CECG results fall behind the 2000-ECG results, but even for the worse case, the ν = 7 state, the difference between the CECG and ECG energies are only by about one in the 8-th significant figure.

In summary, the present tests of CECGs as basis functions in non-BO molecular calculations have shown very good performance of these explicitly-correlated functions. In particular, it is shown that the CECGs are capable to describe the part of the wave function representing the correlated motion of two heavy particles that repel each other. They are also capable to describe excited states of the system in which nodes appear in the wave function in terms of the distance between two heavy repelling particles (in molecules such states correspond to vibrational excitations).

The testing in this work has been performed for rovibrational states corresponding to the zero total rotation quantum number. To describe rotationally excited rovibrational states with CECGs angular factors need to be added as pre-exponential multipliers in a similar way as this was done in the case of the ECGs [17,18]. As in the functional form of the CECGs no distinction is made between the types of particles they are employed to describe and there is no limit, other than the available computer resources, regarding the number of particles in the system which can be considered in the calculation, the ECGs can be applied to perform non-BO calculations of systems no other existing non-BO method is able to calculate. If CECGs are capable of describing a repelling and vibrating pair of heavy particles, as examplified by the proton-deuteron pair of HD⁺ in the non-BO calculations performed in this work, they should also be capable of very accuratelly describing systems which include three or more heavy repelling particles such as H_2^+ , HeH_2^+ , LiH_2^+ , etc. High-accuracy non-BO calculations of the rovibrational spectra of the former two systems that have never been done before are important due to the relevance of these systems to interstellar chemistry.

Table 2

A comparison of the total non-BO energies of the eight lowest bound rovibrational states ($\nu = 0, ..., 7$) of the HD⁺ ion corresponding to the zero total rotational quantum number (N=0) obtained with 1300 CECGs of Eq. (4) with the energies obtained with different number of ECGs of Eq. (4). The number of Gaussians in the basis set used in the calculation is shown for both basis sets. Energies are in hartrees.

ν	No. of Gaussians	Energy	ν	No. of Gaussians	Energy
0	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5978979686 -0.5978979685 -0.5978979686 -0.5978979686	4	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5656110402 -0.5656110418 -0.5656110420 -0.5656110420
1	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5891818295 -0.5891818291 -0.5891818295 -0.5891818295	5	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5585755172 -0.5585755200 -0.5585755206 -0.5585755207
2	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5809037000 -0.5809037001 -0.5809037002 -0.5809037002	6	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5519359402 -0.5519359476 -0.5519359484 -0.5519359486
3	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5730505458 -0.5730505462 -0.5730505464 -0.5730505465	7	1300 CECG 2000 ECG 3000 ECG 4000 ECG	-0.5456859019 -0.5456859137 -0.5456859149 -0.5456859150

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