CHAPTER SEVEN

Nonrelativistic non-Born–Oppenheimer approach for calculating atomic and molecular spectra using all-particle explicitly correlated Gaussian functions

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Contents

Abstract

Very accurate calculations of atomic and molecular spectra require accounting for the coupling of the motions of the nuclei and electrons. To fully account for the nucleus–electron coupling, the nuclei and electrons forming the system have to be treated on an equal footing without assuming the Born–Oppenheimer approximation (non-BO). This can be done by first separating out the Hamiltonian representing the motion of the center of mass from the total nonrelativistic Hamiltonian of the system and then using in the calculation the remaining part of the Hamiltonian that represents the system's internal state. In this work, we review some recent developments of methods by our group for non-BO calculations of atoms and molecules and the results obtained in these calculations. In particular, the review focuses on the challenges of the non-BO calculations and ways to overcome these challenges.

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Abbreviations

BO	Born-Oppenheimer
CEGF	complex explicitly correlated Gaussian function
ECG function	explicitly correlated Gaussian function
Non-BO approach	non-Born-Oppenheimer approach
QED	quantum electrodynamics

1. Introduction

Methods for calculating stationary states of atoms and molecules *without* assuming the Born–Oppenheimer (BO) approximation are being developed for over two decades by the Stanke group at the Nicolaus Copernicus University and by the Adamowicz group at the University of Arizona, and their collaborators.[1–4] The methods allow for very accurate calculations of the spectra of small atoms including the leading relativistic and QED corrections. The non-BO calculations for S, P, D, and F states of atomic systems with 4 and 5 electrons[5–10] are among the most accurate in the literature. Unlike the non-BO methods that employ Gaussian orbitals developed by others,[11–13] our methods employ various types of explicitly correlated all-particles Gaussian (ECG) functions. As ECGs explicitly depend on the distance between the particles (electrons and nuclei), they very efficiently represent their coupled motion and account for the *inter–particle correlation effects*. These effects are indispensable in non-BO calculations, as the Coulombic interactions make particles with like charges avoid each other and particles with opposite charges to follow each other. The correlation effects are particularly strong for the nuclei because, due to their larger masses, they stay apart to a much greater extent than the electrons do. Also, the electrons, particularly the core electrons, follow the nuclei very closely, and this effect can also be also very effectively described by the ECGs.

Without the BO approximation, both isolated atoms and molecules are spherically symmetric systems represented by an internal Hamiltonian, which is spatially isotropic (or atom-like). As the level of the excitation increases, more radial and angular nodes appear in the atomic or molecular non-BO wave function. The are some similarities, as well as differences of the atomic and molecular non-BO wave functions that the ECG basis functions used in the calculation should enable us to describe. In general, an ECG used in a non-BO calculation is a product of two factors, an exponential and a pre-exponential one. The exponent can either be single-centered, $\exp[-\mathbf{r}'\mathbf{A}\mathbf{r}]$, or a multiple-center, $\exp\left[-(\mathbf{r}-\mathbf{s})'\mathbf{A}_k(\mathbf{r}-\mathbf{s})\right]$, Gaussian dependent on the distances between every pair of the N particles (including the reference particle; after separating out the center-of-mass motion, the Hamiltonian representing the internal motion of the system depends on the internal coordinates of $n = N - 1$ pseudoparticles) forming the system, $\mathbf{r}$ being a vector of the internal pseudoparticle coordinates, $\mathbf{A}$ being a symmetric $3n \times 3n$ matrix of exponential parameters, and $\mathbf{s}$ being the vector of the shifts of the Gaussian centers. The Gaussian $\exp[-\mathbf{r}'\mathbf{A}\mathbf{r}]$ can be alternatively represented as follows:

$$\exp\left[-\left(\alpha_1\mathbf{r}_1^2 + \alpha_2\mathbf{r}_2^2 + \cdots + \alpha_n\mathbf{r}_n^2\right) + \left(\beta_{12}\mathbf{r}_{12}^2 + \beta_{13}\mathbf{r}_{13}^2 + \cdots + \beta_{(n-1)n}\mathbf{r}_{(n-1)n}^2\right)\right], \tag{1}$$

where the first part is a product of n orbitals and the second "correlation" part shows the explicit dependency of the Gaussian on the squares of all interparticle distances, $\mathbf{r}_{ij}^2$. The preexponential factor of the Gaussian may include an angular term in the form of a product of Cartesian spherical harmonics and/or powers of the lengths of the internal coordinate vectors.

In a single-center or a multi-center Gaussian, A_k is an $n \times n$ (where $\mathbf{A} = (A_k \otimes I_3)$) symmetric matrix, $\otimes$ is the Kronecker product symbol, and I_3 is a 3×3 identity matrix. In the Gaussians, the exponential parameters are included by the use of a quadratic form involving a vector-matrix-vector product, $\mathbf{r}'(A_k \otimes I_3)\mathbf{r}$. In non-BO calculations of atomic or molecular bound states, the Gaussians have to be square integrable which effectively imposes restrictions on the A_k matrix. The A_k matrix must be positive definite. Rather than restricting the A_k matrix elements, A_k is represented in a Cholesky factored form as: $A_k = L_k L_k'$, where L_k is a lower triangular matrix and its elements can vary from $-\infty$ to $+\infty$. With this representation, A_k is automatically positive definite. It should also be mentioned that this form of A_k matrix does not limit the flexibility of the basis functions since any allowable choice of the A_k matrix can be represented by some L_k matrix. This is because any symmetric positive-definite matrix can be represented in a Cholesky factored form.

As the zero-field nonrelativistic non-BO Hamiltonian commutes with the operators representing the square of the total (electron + nuclei) angular momentum and its projection on a selected axis, the Hamiltonian eigenfunctions have to transform according to irreducible representations of the SO(3) symmetry group of rotations. In particular, the ground-state non-BO molecular wave function is spherically symmetric. In high-precision calculations of isolated atomic and molecular systems, the angular symmetry, as well as permutational symmetries of identical particles, the symmetry properties have to be strictly enforced. If an external perturbation (e.g., interaction with an electric field) is present, the symmetry is lowered and only functions reflecting the new Hamiltonian symmetry have to be included in the basis set. The complexity of the calculation of the properly symmetrized ECG Hamiltonian and overlap matrix elements depends factorially on the numbers of identical particles. Therefore, the application of ECG methods is currently limited to systems with up to 7–8 particles.

Using single-centered (i.e., $\mathbf{s} = \mathbf{0}$) ECGs with real or complex exponential parameters (i.e., the $\mathbf{A}$ matrix is real or we have $\mathbf{A} + i\mathbf{B}$) and with angular factors in the form of products of Cartesian spherical harmonics and with the gradient-based variational algorithms, we have performed very accurate calculations of the spectra of small atoms. The calculations have included the leading relativistic and QED corrections. In particular, the calculations of atomic systems with 4 and 5 electrons should be mentioned, as our non-BO calculations performed for S, P, D, and F states of these systems[5–10] are among the most accurate in the literature.

For calculating ground and excited states of atoms and molecules, one needs to accurately describe radial and angular oscillations of the non-BO wave functions. In particular, the radial oscillations due to vibrational excitations of the molecule require the use of certain types of ECGs. Treating the electrons and nuclei on an equal footing as N particles and after separating out the center of mass from the total nonrelativistic Hamiltonian of the system, the Hamiltonian representing the system's internal motion depends on the n internal coordinates of the $N - 1$ pseudoparticles. We denote by $\mathbf{r} \in \mathbf{R}^n$ the vector of the internal coordinates in the following description:

1. **ECGs with preexponential multipliers** in the form of powers of internuclear distances,

$$\phi(\mathbf{r}) = \prod_i r_i^{m_i} \prod_{i>j} r_{ij}^{m_{ij}} \exp[-\mathbf{r}'\mathbf{A}\mathbf{r}] \qquad \text{(PECG)} \tag{2}$$

   where m_i and m_{ij} are even nonnegative integers, and $\mathbf{A}$ is a real symmetric positive definite $3n \times 3n$ matrix.[14–17]

2. **Complex single-center ECGs** are of the form:

$$\phi(\mathbf{r}) = \exp[-\mathbf{r}'(\mathbf{A} + i\mathbf{B})\mathbf{r}] \qquad \text{(CECG)} \tag{3}$$

   CEGs have been used in Refs. 10,18–21. It has been shown that CECGs are equally if not more efficient than PECGs in describing radial oscillations of excited rovibrational states, even states located near the dissociation threshold.

3. **Real ECGs with shifted centers** are of the form

$$\phi(\mathbf{r}) = \exp[-(\mathbf{r}-\mathbf{q})'\mathbf{A}(\mathbf{r}-\mathbf{q})] \qquad \text{(SECG)} \tag{4}$$

   and have a zero imaginary part $\mathbf{B} = 0$ of the width matrix and a zero momentum vector $\mathbf{p} = \mathbf{0}$. SECGs have been used in Refs. 22–26. Including real shifts in the Gaussians enables us to describe radial oscillations and the angular polarization of the wave function due to, for example, the interaction of the system with the field. These types of deformations can be also described by appropriate spherical harmonics factors, though the shifts may be a more effective way for this task. It should be noted that adding a momentum vector $\mathbf{p}$ is equivalent to introducing a complex shift vector $\mathbf{q}$. The complex shifts allow us to describe ionization/dissociation events that may happen upon high-energy irradiation of an atom or a molecule.

To describe the angular/rotational excitations, ECGs have to be multiplied by products of Cartesian spherical harmonics or by shifting the centers of the Gaussians as it is done in SECGs. Thus, the shifts quite effectively represent both the radial oscillations and the angular polarization of the wave function.

The fully complex ECGs enable the accurate description of the following features of the non-BO wave function: (a) the electron–electron, electron–nucleus, and nucleus–nucleus correlation effects; (b) the angular and radial polarization and oscillation caused by the interaction with laser pulses with variable frequencies and intensities; and (c) ionization/dissociation of the system. With complex matrix $\mathbf{C}_k$ and complex shift vectors $\mathbf{s}_k$, i.e., $\mathbf{C}_k = \mathbf{A}_k + \mathrm{i}\mathbf{B}_k$ and $\mathbf{s}_k = \mathbf{z}_k + \mathrm{i}\mathbf{w}_k$, where $\mathbf{z}_k$ and $\mathbf{w}_k$ are real vectors, $\phi_k(\mathbf{r})$ has the form:

$$\phi_k(\mathbf{r}) = \exp[-(\mathbf{r}-\mathbf{s}_k)'(\mathbf{A}_k + \mathrm{i}\mathbf{B}_k)(\mathbf{r}-\mathbf{s}_k)], \tag{5}$$

where $\mathbf{r}$ is the vector of the Cartesian internal coordinates of the particles forming the system, $\mathrm{i} = \sqrt{-1}$ and $'$ denotes vector/matrix transposition. An alternative, but equivalent, form of $\phi_k(\mathbf{r})$ is:

$$\phi_k(\mathbf{r}) = \exp[-(\mathbf{r}-\mathbf{z}_k)'(\mathbf{A}_k + \mathrm{i}\mathbf{B}_k)(\mathbf{r}-\mathbf{z}_k) + \mathrm{i}\mathbf{w}_k'\mathbf{r}]. \tag{6}$$

Recent work[27] has shown that such complex Gaussians possess sufficient flexibility to describe the time-evolving state of an atom or molecular system subject to strong and short laser pulses with variable frequencies and intensities. The presence of the plane-wave component in the Gaussians allows the description of the ionization/dissociation dynamics.

2. Separation of the center-of-mass motion from the total nonrelativistic Hamiltonian of the system

As the number-crunching power of computers keeps growing over the years, it becomes possible, at least for the smallest molecular systems, to reduce the number of approximations to a minimum. In the approach adopted in this work, we consider few-electron diatomic systems, LiH and LiH$^-$, without the use of the Born–Oppenheimer approximation. This means that all particles, i.e., the nuclei and electrons forming the molecule, are treated on an equal footing. Such an approach, if it only concerns the internal bound states of the system, necessitates that the center-of-mass motion is removed from the Hamiltonian. This separation in the non-BO method we have developed is done by starting with the total nonrelativistic Hamiltonian of the molecule written in terms of laboratory Cartesian coordinates representing the kinetic and potential energies of the nuclei and the electrons. The general lab-frame nonrelativistic all-particle Hamiltonian of a system of N particles (N being a sum of the number of nuclei and the number of electrons) in atomic units is represented by operator:

$$H_{\mathrm{nr}}^{\mathrm{lab}} = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2M_i} + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{Q_i Q_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \tag{7}$$

where M_i, Q_i, $\mathbf{R}_i$, $\mathbf{P}_i$ are the mass, charge, the Cartesian coordinates, and the corresponding linear momenta of the ith particle, respectively. The following nuclear masses are used in the present calculations: $M(^1\mathrm{H}) = 1836.15267389 m_e$, $M(^2\mathrm{H}) = 3670.48296785 m_e$, $M(^6\mathrm{Li}) = 10961.89865 m_e$, $M(^7\mathrm{Li}) = 12786.39228 m_e$, $M(^9\mathrm{Be}) = 16424.2055 m_e$, $M(^{10}\mathrm{B}) = 18247.46879 m_e$, $M(^{11}\mathrm{B}) = 20063.73729 m_e$, $M(^{14}\mathrm{N}) = 25519.045282 m_e$, and $M(^{15}\mathrm{N}) = 27336.528712 m_e$, where mass of electron $m_e = 1$.

Next, Hamiltonian (7) is expressed in terms of new Cartesian coordinates that comprise the three lab-frame coordinates describing the position of the system's center of mass in laboratory Cartesian coordinate frame and the remaining $3N - 3$ coordinates that are internal coordinates. In our approach, the internal coordinates $\mathbf{r}_{i-1} = \mathbf{R}_i - \mathbf{R}_1$ are the Cartesian coordinates of vectors with the origins at a chosen reference particle located at $\mathbf{R}_1$ (usually the heaviest nucleus in the system, which we can call particle 1) and ending at the positions of particles 2, 3, …, N. A transformation of the total nonrelativistic Hamiltonian to the new coordinates system results in its rigorous separation of the lab-frame Hamiltonian into an operator that represents the kinetic energy of the center-of-mass motion and an internal Hamiltonian, as described in the next section. The center-of-mass kinetic energy Hamiltonian depends only on the center-of-mass laboratory coordinates and the internal Hamiltonian depends only on the internal coordinates.[28]

As mentioned, the nonrelativistic calculations in the present work are carried out using a Hamiltonian that represents the internal state of the molecule and excludes the motion of the center of mass, i.e., excludes the translational motion of the system as a whole. The internal Hamiltonian expressed in terms of the internal Cartesian coordinates, $\mathbf{r}_i$, $i = 1, \ldots, n$, where $n = N - 1$ and N is the number of particles (electrons and nuclei) forming the molecule, is as follows[28]:

$$\hat{\mathrm{H}} = -\frac{1}{2}\left(\sum_{i=1}^{n} \frac{1}{\mu_i} \nabla'_{\mathbf{r}_i} \nabla_{\mathbf{r}_i} + \frac{1}{m_0} \sum_{\substack{i,j=1 \\ i \neq j}}^{n} \nabla'_{\mathbf{r}_i} \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^{n} \frac{q_0 q_i}{r_i} + \sum_{i>j=1}^{n} \frac{q_i q_j}{r_{ij}}, \qquad (8)$$

where m_0 is the mass of the reference nucleus (in the present calculations, the lithium nucleus) and q_0 is its charge, q_i are the charges of the other particles, $\mu_i = m_0 m_i / (m_0 + m_i)$ is the reduced mass of particle i (m_i, $i = 1, \ldots, n$, are the particle masses), $r_i = |\mathbf{r}_i|$, $i = 1, \ldots, n$ is the distance from particle $n + 1$ to the reference particle, i.e., particle 1, and r_{ij} is the distance between particle $j + 1$ and particle $i + 1$. The prime symbol in (8) denotes the matrix/vector transposition. One can notice that the internal Hamiltonian represents the motion of n particles, whose charges are the original particle charges, but the masses are the reduced masses (because of that, one can use the term "pseudoparticles" to denote the particles described by the internal Hamiltonian (8)), in the central field of the charge of the reference nucleus. Thus, the internal Hamiltonian is invariant upon all rotations around the center of the internal coordinate system and one can think of it as an "atom-like" Hamiltonian. The eigenfunctions of this Hamiltonian can be classified using the same symmetries as the wave functions of atoms. These eigenfunctions and the corresponding eigenvalues (energies) represent all modes of the internal motions of the molecule including the electronic, vibrational, and rotational motions. In particular, the ground-state solution is spherically symmetric, i.e., it is invariant under rotations in 3D.

The approach used to obtain the internal Hamiltonian (8) and to separate out the center-of-mass motion from the lab-frame Hamiltonian is a generalization of the standard textbook approach used to reduce a two-body problem to a one-body problem in quantum mechanics, e.g., in the case of an electron and proton forming the hydrogen atom.

3. Generation of the Basis set in a non-BO calculation

The calculations described in this work are performed using the Rayleigh–Ritz variational scheme involving minimization of the Rayleigh quotient:

$$E(\mathbf{a};\mathbf{c}) = \min_{\{\mathbf{a},\mathbf{c}\}} \frac{\mathbf{c}' H(\mathbf{a})\mathbf{c}}{\mathbf{c}' S(\mathbf{a})\mathbf{c}}, \tag{9}$$

where $H(\mathbf{a})$ is the matrix of the internal Hamiltonian H, $S(\mathbf{a})$ is the overlap matrix, and $\mathbf{c}$ is a vector of the linear expansion coefficients of the wave function in terms of the basis functions. Notation $E(\mathbf{a};\mathbf{c})$ indicates that the energy depends on the nonlinear parameters of the basis functions (the $\mathbf{a}$ vector) and on the $\mathbf{c}$ coefficients (the $\mathbf{c}$ vector).

In the variational energy minimization, the matrix elements of the L_k matrices of the Gaussians (and the coordinates of the Gaussian shifts, $\mathbf{s}_k$, in the case of shifted Gaussians) that form vector a are fully optimized. Generating the basis set for the lowest-energy state of a particular spin/spatial symmetry is initiated with a small, randomly chosen set of functions and involves incremental addition of new functions and variationally optimizing them with an approach employing the analytic energy gradient. The new functions are added to the basis set one by one with L_k parameters chosen as a best guess out of several hundred candidates. The parameters of the candidate functions are generated based on the parameters of the functions already included in the set. After a new function is selected, its i_k electron number index and the L_k parameters are optimized. Next the function is checked for any linear dependency with the functions already included in the basis set and, if such linear dependency appears, the function is rejected and replaced by a new function. This new function is then subject to optimization. After a certain number of new functions (usually a hundred) are added to the basis set, the whole set is reoptimized by cycling over all functions one by one and reoptimizing their L_k parameters. After the parameters of a function are reoptimized, the function is again checked for any linear dependency with all other functions in the set, and its parameters are reset to their original values if the linear dependency within a certain predefined threshold occurs. The cyclic optimization of all functions is usually repeated several times. The process of basis set growing continues until satisfactory convergence is reached for each state.

The optimization of a basis set for the second lowest state of the system is initiated with a basis set generated for the lowest-energy state. Usually, that basis set is significantly smaller than the largest basis set generated for this state, but still provides reasonably good representation in terms of the state's energy and the wave function of the state. In the optimization of the basis set for the second lowest state, the initial basis is augmented by additional functions which are reoptimized along with the functions contained in the initial basis set to obtain a well-converged solution (i.e., the energy and the wave function) for the state. A similar procedure is applied to obtain the energy and the wave function for the third-lowest energy state. In this case, the optimization is initiated using a basis set generated for the second-lowest energy state.

A unique feature of our approach is the use of the analytically calculated first derivatives of the energy functional determined with respect to the nonlinear Gaussian parameters in their optimizations. The derivatives that form the gradient vector are determined as:

$$\partial_{\mathbf{a}} E = \frac{1}{\mathbf{c}' S \mathbf{c}} \left(\frac{\partial \mathrm{vech} H}{\partial \mathbf{a}'} - E \frac{\partial \mathrm{vech} S}{\partial \mathbf{a}'} \right)' (\mathrm{vech}[2\mathbf{c}\mathbf{c}' - \mathrm{diag}\,\mathbf{c}\mathbf{c}']), \tag{10}$$

where vech is an operation that forms a $m(m+1)/2$-dimensional vector (m is the number of the basis functions) of unique matrix elements of a symmetric matrix. The use of the energy gradient in the minimization of the energy functional considerably accelerates the convergence of the optimization process.

4. Examples of non-BO atomic and molecular calculations

For atomic states with all s electrons, such as ^{1}S states of the beryllium atom, Gaussians $\exp[-\mathbf{r}'\mathbf{A}\mathbf{r}]$ are used. For atomic states with one p electron and the remaining electrons being s electrons, such as ^{2}P states of the lithium and boron atoms, the Gaussians are: $z_i \exp[-\mathbf{r}'\mathbf{A}\mathbf{r}]$, where z_i is the z coordinate of the i electron.

For atomic states with three p electrons, such as for ^{4}S states of the nitrogen atom, the basis functions can be obtained by coupling together their angular momenta using the appropriate Clebsch–Gordan coefficients. Thus, a linear combination of the following nonnormalized forms of spherical harmonic functions $Y_1^0 = z_i$, $Y_1^1 = 1/\sqrt{2}(x_i + iy_i)$, and $Y_1^{-1} = 1/\sqrt{2}(x_i - iy_i)$ expressed in the Cartesian coordinates where the common constant factor and the $1/r_i^{l_i}$ factor were dropped (l_i is the angular momentum quantum number of the ith electron) is generated. Let us suppose that the orbital quantum numbers of electrons i, j, and k (k in this case is not the index for the basis function expansion but an electron index) are l_i, m_i, l_j, m_j, l_k, and m_k. Using the bracket notation, the angular part of the basis function corresponding to particular L and M can be represented as the following linear combination:

$$|L\ M\rangle = \sum_{\substack{m_i,\, m_j,\, m_k \\ m_i + m_j + m_k = M}} (L\ M|l_i\ m_i\ l_{jk}\ m_{jk})(l_{jk}\ m_{jk}|l_j\ m_j\ l_k\ m_k)|l_i\ m_i\rangle|l_j\ m_j\rangle|l_k\ m_k\rangle, \tag{11}$$

where the $\left(L\ M|l_i\ m_i\ l_{jk}\ m_{jk}\right)$ and $\left(l_{jk}\ m_{jk}|l_j\ m_j\ l_k\ m_k\right)$ factors are the Clebsch–Gordan coefficients.[29] With that, the angular part of the basis function for a state of three p electrons with $L = 0$ and $M = 0$ becomes:

$$\left(x_j y_i - x_i y_j\right) z_k + \left(x_i y_k - x_k y_i\right) z_j + \left(x_k y_j - x_j y_k\right) z_i, \tag{12}$$

where again the $1/(r_i^{l_i} r_j^{l_j} r_k^{l_k})$ factor was dropped. Therefore, the full form of the basis function $\phi_k(\mathbf{r})$ is obtained by multiplying together $\exp[-\mathbf{r}'\mathbf{A}_k\mathbf{r}]$ and the angular component (12):

$$\begin{aligned}
\psi_k(\mathbf{r}) &= \left\{ \left(x_{j_k} y_{i_k} - x_{i_k} y_{j_k}\right) z_{k_k} + \left(x_{i_k} y_{k_k} - x_{k_k} y_{i_k}\right) z_{j_k} + \left(x_{k_k} y_{j_k} - x_{j_k} y_{k_k}\right) z_{i_k} \right\} \exp\left[-\mathbf{r}'\mathbf{A}_k\mathbf{r}\right] \\
&= \left(\mathbf{r}'\mathbf{v}_k^{x_j}\right)\left(\mathbf{r}'\mathbf{v}_k^{y_i}\right)\left(\mathbf{r}'\mathbf{v}_k^{z_k}\right) - \left(\mathbf{r}'\mathbf{v}_k^{x_i}\right)\left(\mathbf{r}'\mathbf{v}_k^{y_j}\right)\left(\mathbf{r}'\mathbf{v}_k^{z_k}\right) + \left(\mathbf{r}'\mathbf{v}_k^{x_i}\right)\left(\mathbf{r}'\mathbf{v}_k^{y_k}\right)\left(\mathbf{r}'\mathbf{v}_k^{z_j}\right) \\
&\quad - \left(\mathbf{r}'\mathbf{v}_k^{x_k}\right)\left(\mathbf{r}'\mathbf{v}_k^{y_i}\right)\left(\mathbf{r}'\mathbf{v}_k^{z_j}\right) + \left(\mathbf{r}'\mathbf{v}_k^{x_k}\right)\left(\mathbf{r}'\mathbf{v}_k^{y_j}\right)\left(\mathbf{r}'\mathbf{v}_k^{z_i}\right) \\
&\quad - \left(\mathbf{r}'\mathbf{v}_k^{x_j}\right)\left(\mathbf{r}'\mathbf{v}_k^{y_k}\right)\left(\mathbf{r}'\mathbf{v}_k^{z_i}\right) \exp\left[-\mathbf{r}'\mathbf{A}_k\mathbf{r}\right].
\end{aligned} \tag{13}$$

In the above, vector–vector products are used to replace the angular Cartesian coordinates. These replacements allow for a more generalized approach in deriving the expressions for the Hamiltonian matrix elements. The vectors $\mathbf{v}_k^{x_i}$, $\mathbf{v}_k^{y_i}$, $\mathbf{v}_k^{z_i}$, $\mathbf{v}_k^{x_j}$, $\mathbf{v}_k^{y_j}$, $\mathbf{v}_k^{z_j}$, $\mathbf{v}_k^{x_k}$, $\mathbf{v}_k^{y_k}$, and $\mathbf{v}_k^{z_k}$ used in (13) are sparse $3n$ vectors comprising of only one element of a nonzero value of "1" in the position describing the nonzero-angular-momentum particle and its angular coordinate. Note that $\mathbf{v}_k$ vectors cannot be represented as a Kronecker product of an n-component vector v_k with I_3: $\mathbf{v}_k \neq v_k \otimes I_3$.

Before ECGs are used to expand the wave function of the considered state of the system, they have to be appropriately permutation-symmetry adapted. In the present approach, we use the spin-free formalism for this adaptation. The approach involves construction of a permutation-symmetry projector using the standard procedure based on Young operators. In the case of the doublet states of lithium, the singlet states of beryllium, the doublet states of boron, and the quartet states of the nitrogen, the corresponding Young operators are chosen as (particle one is the nucleus and particles 2, 3, … are the electrons):

$(1 + P23)(1 - P34)$,
$(1 - P24)(1 - P35)(1 + P23)(1 + P45)$,
$(1 - P24)(1 - P26 - P46)(1 - P35)(1 + P23)(1 + P45)$, and
$(1+P56)(1+P78)(1-P68)(1-P57)(1-P27-P25)(1-P23-P37-P35)$
$(1-P34-P24-P47-P45)$, respectively, where the Pij operator permutes the labels of the i and j electrons. More details about the implementation of the Young-operator approach in our calculations can be found in Ref. 30.

It should be noted that the variational optimization of the ECG exponential parameters is only carried out for the wave functions of the leading isotope of the atom (e.g., the ^{7}Li isotope of the lithium atom). In the calculations of the other isotopes and in the infinite-nuclear-mass calculations, the basis sets generated for the leading isotopes are used without reoptimization of their nonlinear parameters. Our experience with atomic calculations has shown that adjusting the linear expansion coefficients, c, provides a sufficiently accurate way to account for a relatively small change of the wave function caused by the change in the nuclear mass.

These are the following bound states of four atomic systems considered in the calculations performed in this work: the lowest twelve ^{2}P states of the lithium atom, the lowest ten ^{1}S states of the beryllium atom, the lowest nine ^{2}P states of the boron atom, and five ^{1}S states of the nitrogen atom. For all the considered states, except for some lowest states of the lithium atom (for these states, calculations performed with explicitly correlated Slater functions produced slightly better energies than those obtained with Gaussians) the total variational energies obtained in the calculations are the lowest ever obtained in ab initio calculations for these systems. The optimizations of the ECG basis sets for each atom are performed for the leading isotope of that atom. The generated basis are subsequently used in the calculations of other stable isotopes of each atom, as well as for an atom with an infinite nuclear mass. The results for the ^{2}P states of the ^{6}Li, ^{7}Li, and $^{\infty}$Li isotopes of the lithium atom are shown in Table 1, the results for the ^{1}S states of the ^{9}Be and $^{\infty}$Be isotopes of the beryllium atom are shown in Table 2, the results for the

Table 1 The total nonrelativistic non-BO energies E_{nrel} of the $n\ ^{2}P$ states of isotopes of the lithium atom ^{6}Li, ^{7}Li, $^{\infty}$Li, where $n = 2, 3, \ldots, 13$.

State	Basis	^{6}Li	^{7}Li	$^{\infty}$Li
$2\ ^{2}P$	17,000	−7.409 458 110 577	−7.409 557 759 019	−7.410 156 532 650
$3\ ^{2}P$	13,100	−7.336 457 285 733	−7.336 556 363 709	−7.337 151 708 591
$4\ ^{2}P$	14,000	−7.311 196 254 262	−7.311 295 101 661	−7.311 889 060 748
$5\ ^{2}P$	14,000	−7.299 596 170 656	−7.299 694 902 379	−7.300 288 166 250
$6\ ^{2}P$	14,000	−7.293 328 522 041	−7.293 427 187 815	−7.294 020 055 325
$7\ ^{2}P$	15,500	−7.289 563 667 252	−7.289 662 291 968	−7.290 254 912 721
$8\ ^{2}P$	16,000	−7.287 127 026 011	−7.287 225 623 467	−7.287 818 080 395
$9\ ^{2}P$	16,000	−7.285 460 106 102	−7.287 225 623 467	−7.286 151 027 247
$10\ ^{2}P$	17,000	−7.284 269 825 426	−7.284 368 390 101	−7.284 960 650 009
$11\ ^{2}P$	17,000	−7.283 390 376 949	−7.283 488 931 330	−7.284 081 129 330
$12\ ^{2}P$	17,000	−7.282 722 235 788	−7.282 820 782 270	−7.283 412 932 799
$13\ ^{2}P$	17,000	−7.282 300 479 312		−7.284 079 728 671

All values in hartrees.

Table 2 The total nonrelativistic non-BO energies E_{nrel} of the $n\ ^{1}S$ states of isotopes of the beryllium atom ^{9}Be and $^{\infty}$Be, where $n = 2, 3, \ldots, 11$.

State	Basis	^{9}Be	$^{\infty}$Be
$2\ ^{1}S$	16,000	−14.666 435 526 317	−14.667 356 508 387
$3\ ^{1}S$	16,000	−14.417 335 144 083	−14.418 240 368 939
$4\ ^{1}S$	16,000	−14.369 185 514 672	−14.370 087 938 507
$5\ ^{1}S$	16,000	−14.350 610 429 797	−14.351 511 737 910
$6\ ^{1}S$	16,000	−14.341 502 934 723	−14.342 403 688 992
$7\ ^{1}S$	16,000	−14.336 366 130 065	−14.337 266 570 323
$8\ ^{1}S$	17,000	−14.333 186 043 180	−14.334 086 288 670
$9\ ^{1}S$	17,000	−14.331 080 947 170	−14.331 981 063 789
$10\ ^{1}S$	17,000	−14.329 614 861 820	−14.330 514 888 895
$11\ ^{1}S$	17,000	−14.328 550 996 542	−14.329 450 958 909

All values in hartrees.

Table 3 The total nonrelativistic non-BO energies E_{nrel} of the of $n\,^2P$ states of isotopes of the boron atom ^{10}B, ^{11}B, $^{\infty}$B, where $n = 2, 3, \ldots, 10$.

State	Basis	^{10}B	^{11}B	$^{\infty}$B
$2\,^2P$	16,000	−24.652 502 680 636	−24.652 626 315 397	−24.653 868 525 181
$3\,^2P$	16,000	−24.430 973 916 386	−24.431 097 899 360	−24.432 343 606 383
$4\,^2P$	16,000	−24.389 170 171 127	−24.389 294 047 421	−24.390 538 682 291
$5\,^2P$	16,000	−24.372 547 534 026	−24.372 671 358 362	−24.373 915 471 635
$6\,^2P$	16,000	−24.364 219 865 377	−24.364 343 660 569	−24.365 587 486 912
$7\,^2P$	16,000	−24.359 451 263 777	−24.359 575 039 883	−24.360 818 693 430
$8\,^2P$	16,000	−24.356 464 432 488	−24.356 588 195 903	−24.357 831 737 404
$9\,^2P$	16,000	−24.354 455 451 626	−24.354 579 209 823	−24.355 822 673 751
$10\,^2P$	16,000	−24.353 024 913 107	−24.353 148 632 914	−24.354 392 079 994

All values in hartrees.

Table 4 The total nonrelativistic non-BO energies E_{nrel} of the of $n\,^2P$ states of isotopes of the nitrogen atom ^{14}N, ^{15}N, $^{\infty}$N, where $n = 2, 3, \ldots, 6$.

State	Basis	^{14}N	^{15}N	$^{\infty}$N
$2\,^2P$	128	−54.548 106 795 683	−54.548 244 637 939	−54.550 180 140 287
$3\,^2P$	128	−54.070 292 960 572	−54.070 430 919 917	−54.072 368 063 483
$4\,^2P$	128	−53.899 406 696 128	−53.899 541 400 451	−53.901 432 831 328
$5\,^2P$	244	−53.701 687 058 152	−53.706 202 762 186	−53.708 150 318 836
$6\,^2P$	256	−53.122 252 189 699	−53.122 388 837 119	−53.124 306 684 080

All values in hartrees.

^{2}P states of the ^{10}B, ^{11}B, and $^{\infty}$B isotopes of the boron atom are shown in Table 3, and the results for the ^{1}S states of the ^{14}N and $^{\infty}$N isotopes of the nitrogen atom are shown in Table 4. An example of non-BO molecular calculations shown in this work concerns all bound states of the HD$^+$ ion corresponding to the zero total angular momentum. There are 23 such states and they correspond to what is conventionally called the "pure vibrational excitations." However, due to the coupling of the motion of the nuclei and the motion of the electrons that occurs when the system is described without assuming the Born–Oppenheimer approximation, the vibrational quantum number is not, strictly speaking, a good quantum number. The challenge in calculating all 23 bound "vibrational" states of HD$^+$ with comparable accuracy is due to the need of describing the radial oscillations of the wave functions of these states with equal accuracy. Two approaches are used for this purpose in this work. In the first one, PECGs are used, and in the second one, CECGs are used. The results obtained with these two basis sets are compared in Table 5.

Table 5 The total nonrelativistic non-BO energies of the pure vibrational states of HD^+.

ν	Basis	E_{nrel}	ν	Basis	E_{nrel}	ν	Basis	E_{nrel}
0	1700	−0.597 897 968 59	1	1649	−0.589 181 829 50	2	1700	−0.580 903 700 14
	*1500	−0.597 897 968 58		*1500	−0.589 181 829 51		*1600	−0.580 903 700 12
3	1780	−0.573 050 546 41	4	1700	−0.565 611 041 73	5	1840	−0.558 575 520 39
	*1500	−0.573 050 546 31		*1600	−0.565 611 041 61		*1700	−0.558 575 520 19
6	1740	−0.551 935 947 94	7	1740	−0.545 685 913 88	8	1865	−0.539 820 639 73
	*1700	−0.551 935 947 84		*1700	−0.545 685 913 57		*1700	−0.539 820 638 67
9	1865	−0.539 820 639 73	10	1900	−0.534 337 010 93	11	1820	−0.529 233 630 55
	*1700	−0.534 337 009 15		*1700	−0.529 233 628 50		*1700	−0.524 510 900 41
12	1800	−0.524 510 903 52	13	1800	−0.520 171 138 12	14	1800	−0.516 218 695 97
	*1700	−0.520 171 133 16		*1600	−0.516 218 684 23		*1600	−0.512 660 156 98
15	1800	−0.512 660 174 92	16	1800	−0.509 504 625 62	17	1800	−0.506 763 848 46
	*1600	−0.509 504 603 52		*1600	−0.506 763 816 14		*1600	−0.504 452 626 59
18	1800	−0.504 452 661 84	19	1800	−0.502 589 190 42	20	1860	−0.501 194 759 49
	*1600	−0.502 589 154 43		*1600	−0.501 194 710 60		*1600	−0.500 292 362 14
21	1940	−0.500 292 416 44	22	1980	−0.499 910 347 15	23	2000	−0.499 865 774 69
	*1700	−0.499 910 332 87		*1700	−0.499 865 770 26			

The result marked with * are taken from Ref. 31. All values in hartrees.

As one can see, results obtained with the two basis sets are almost equally accurate with, perhaps, the PECG results being slightly better than the CECG result—an effect which can be attributed to the larger sizes of the PECG basis sets.

5. Challenges of non-BO calculations

The computer time for an all-particle non-BO calculation scales as a product of the factorials of the numbers of identical particles. For an atom, the scaling factor is the factorial of the number of the electrons. The scaling is due to the number of terms in the permutation-symmetry operator which for an atom with n electrons is equal to $n!$. Thus, each H or S matrix element is a sum of $n!$ corresponding elemental integrals. The $n!$ time scaling is the major bottleneck of a non-BO calculation will all-particle ECGs.

Another size-limiting step in the non-BO calculation is the solution of the secular equation used to determine the energy and the linear expansion coefficients of the wave function. At this point, our effort is particularly focused on creating a procedure for a very fast one-root eigen-problem solver for complex all-particle ECGs.

6. Summary and future directions

In this work, the procedure for performing non-BO calculations of small atoms and molecules with all-particle explicitly correlated Gaussian functions developed in our laboratories is described. The procedure is used to calculate some Rydberg states of the lithium, beryllium, boron, and nitrogen atoms. The basis sets generated for the leading isotope of each atom are used to calculate energies and wave functions of other stable isotopes of the atom, as well as the energy of the atom with an infinite nuclear mass. The results of the calculations can be used to calculate the isotope energy shifts. Some bottlenecks of the non-BO calculations are discussed.

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