CHAPTER FIVE

# Treating the motion of nuclei and electrons in atomic and molecular quantum mechanical calculations on an equal footing: Non-Born–Oppenheimer quantum chemistry

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### Abstract

The Born–Oppenheimer (BO) approximation is the bedrock of quantum mechanical calculations of atomic and molecular systems. However, there are effects in these systems that require departure from the BO approximations. We start this review with describing these effects and some of the previous works where calculations were performed to account for their magnitude in various atomic and molecular properties. In particular, the problem of selecting appropriate basis functions for non-BO calculations is analyzed and some examples of such calculations are presented. The last part of this review is devoted to perspectives in carrying out quantum mechanical studies of structures, spectra, and other properties of atoms and molecules in isolation and in confinement and treating both nuclei and electrons in these studies on on equal footing.

# 1. Introduction

Even though the application of the quantum mechanics to study bound ground and excited states of atomic and molecular systems has been solidly based on the Bon–Oppenheimer (BO) approximation, there has been considerable interest in obtaining quantum mechanical description of these systems without assuming the approximation.<sup>1–3</sup> There are several reasons for departing from the BO approximations in the calculations of bound states of atoms and molecules. Some of these reasons are mentioned below.

From the very beginning of the atomic and molecular quantum mechanics development of theoretical models that produce results agreeing with the most up-to-date high-resolution spectroscopy measurements performed on light atomic and molecular has been an important part of research. It has allowed validation of the existing models and development of better ones. As the experimental techniques advance and achieve higher levels of precision, refinements have been made in the theoretical models to describe effects and interactions neglected (or treated more approximately) in the previous models. In recent years, the accuracy of measuring such quantities as molecular rovibrational transition energies, ionization potentials, electron affinities, and fine and hyperfine splitting has achieved the precision of  $0.01-0.001 \text{ cm}^{-1}$ . The breadth and accuracy of the experimental data have been increasing rapidly and further major improvements are expected due to the development of new experimental methods for UV laser generation and frequency metrology with phase-locked femtosecond combs.<sup>4</sup> The data collected using those new techniques are beginning to reveal deviations that suggest that the accuracy of the existing calculations is no longer adequate.

Achieving the 0.01–0.001 cm<sup>-1</sup> precision in the theoretical calculations requires the inclusion of effects reaching beyond the second-order in the fine structure constant  $\alpha = \frac{1}{c}$  and the effects due to the finite structures of the nuclei. These types of effects have already been calculated for two- and three-electron atomic systems leading to theoretical results which are very precise.<sup>5–13</sup> Now the challenge is to extend these types of calculations to small molecular systems with more than two nuclei. New high-precision theoretical results for such systems, when compared with new more exact experimental values, will provide new grounds for validation of the theoretical models and for the assessment of their limitations.

The development of high-end quantum mechanical methods has always been an important source of ideas and technical solutions for the development of less accurate approaches which can be applied to larger systems. The constantly increasing power of computers has made possible to extend the use of techniques developed for small systems to larger systems. For example, the use of so-called explicitly correlated basis functions for expanding the electronic wave function of the system becomes increasingly popular. In particular, the techniques related to the use of explicitly correlated Gaussian (ECG) functions in atomic and molecular calculations featured in this article, such as, for example, the techniques of employing analytical derivatives of the energy with respect to the Gaussian exponential parameters in the variational energy minimization and in the optimizations of the basis functions, have already been utilized by our group in less accurate BO and non-BO calculations for larger molecules.<sup>14–17</sup> As the correlated Gaussians will start to replace Gaussian orbitals as basis functions in expanding correlated wave functions in high-end molecular BO calculations, these techniques may find new applications. For example, further development of such approaches as the R12 (or F12) method of Kutzelnigg et al.<sup>18</sup> may benefit from utilizing the analytical gradient technique. Another example is the use of the ECGs with time-dependent nonlinear parameters (e.g., Gaussian centers) in studying the dynamics of chemical processes such as, for example, processes initiated by photo-excitations in clusters. The non-BO methods can also provide useful tools for the development of methods for describing the dynamics of the coupled nucleus-electron motion in atomic and molecular systems. This phenomenon can now be studied experimentally with the femto- and attosecond spectroscopies.

When the BO approximation is not assumed in nonrelativistic atomic or molecular calculations, the wave functions and the corresponding nonrelativistic energy levels explicitly include effects originating from the finite masses of the nuclei and from the coupling of the motions of the nuclei and electrons. If such non-BO wave functions are then 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. This contributes to the enhancement of the calculation accuracy. We have showed that such an approach can produce results whose accuracy match the accuracy of the most accurate experimental measurements.<sup>3</sup>

The interest in carrying out the non-BO atomic and molecular calculations also stems from the strive to describe various properties and structures of molecules and atoms with quantum mechanical calculations where all particles forming the system are treated equivalently. With that the structural parameters of the molecule, the dipole moment, polarizabilities, etc., are calculated as expectation values of operators representing these properties using the non-BO wave functions. In such calculations (see, for example, Ref. 19), for molecules containing identical nuclei, the indistinguishability principle leads to interesting effects not present in the calculations performed based on the BO approximation, where identical nuclei are distinguishable. For example, according the quantum mechanics, in order to determine the structure of a molecule one needs to calculate the expectation values of the geometrical parameters (i.e., internuclear distances and angles) using the non-BO wave function. If this is done for a molecule with identical nuclei, e.g.,  $H_3^+$  or  $H_3$ , as we did in Ref. 19, one only obtains a single bond-distance value, which for  $H_3^+$  is an average of the three internuclear distances, i.e., the distance between proton one and proton two, the distance between proton two and proton three, and the distance between proton three and proton one (and analogically only one bond angle). Based on a single internuclear distance and a single angle one cannot determine the molecular structure of  $H_3^+$ . The same happens for electrons. Let us consider a molecule with three electrons. Due to indistinguishability, if one takes a properly antisymmetrized electronic wave function and calculates the interelectron distances, one only obtains a single value, not three values. So the "structure of the electrons in the molecule," analogically to the structure of the protons (i.e., the molecular structure) cannot be determined. If one treats the nuclei and the electrons on an equal footing, as happens in the non-BO calculations, similar effects appear for both types of particles.

In our works concerning the use of ECGs, both BO and non-BO approaches have been employed. Despite the fact that both these approaches are based on the principles of quantum mechanics, there are significant differences in the way the calculations are carried out using the approaches. For example, in order to determine the rovibrational spectrum of a molecule within the BO approximation, one needs to perform separate calculations of the electronic wave functions and the corresponding energies at some selected molecular geometries (i.e., configurations of the nuclei) where the nuclei are placed in different fixed positions in space. These calculations yield the so-called potential energy surface (PES), which is subsequently used to calculate the rovibrational states of the molecule by solving the nuclear-motion Schrödinger equation where the PES is used as the potential energy operator. In the non-BO approach, as the nuclei and the electrons forming the molecule are treated on equal footing, the calculations yield

the total energies and the corresponding total wave functions, which explicitly depend on the coordinates of both nuclei and electrons. Both the energies and wave functions directly include all effects (including the high-order ones) that originate from the coupling of the motion of the nuclei and the motion of the electrons, i.e., adiabatic and nonadiabatic effects. Thus, there is no separation between the electronic wave function and the rovibrational nuclear wave function. The total non-BO wave functions, besides being eigenfunctions of the Hamiltonian, are also eigenfunctions, of the square of the total angular momentum operator and its projection on the z-axis. They are also eigenfunctions of the corresponding total spin operators  $(S^2 \text{ and } S_z)$ . They represent the states of the systems that only approximately can be assigned particular vibrational and nuclear rotational quantum numbers (more on this later is this article).

The "good" quantum numbers, which can be used to label the eigenstates of the non-BO nonrelativistic Hamiltonian that describes the internal state of the system (see the next section), are the quantum numbers that quantize the square of the total angular momentum and its projection on the *z*-axis (also the quantum numbers that quantize the eigenvalues of  $S^2$  and  $S_z$ ). As the Hamiltonian is isotropic (i.e., invariant with respect to rotations about the center of the internal coordinate system described later in this work) the wave functions are atom-like (i.e., they transform according to the irreducible representations of the SO(3) rotation group). It is convenient to use basis functions that are eigenfunctions of the square of the total orbital angular momentum and its projection on the *z*-axis in the non-BO calculations because then the problem of calculating atomic or molecular bound states separates into independent calculations, each corresponding to states with different total-orbital-angular-momentum quantum number and its *z*-axis projection quantum number.

### 2. Separating out the center-of-mass motion

The starting point of our non-BO approach for non-BO atomic and molecular calculations is the total nonrelativistic Hamiltonian that depends on laboratory-frame Cartesian coordinates of all particles forming the system. This Hamiltonian describes two types of motion. The first part is the motion of the particles around the center of mass of the system. We call this motion the internal motion. The second type of motion is the translational motion of the center of mass in 3D space. If the system is isolated, the motion of the system as a whole, i.e., the second type of motion, has a continuous (i.e., nondiscrete) energy spectrum. If the system is placed in some-type of a confining potential well (e.g., in a magnetic trap), the whole or a part of the energy spectrum becomes discrete (quantized). The spectrum of the internal states of the system may have a part which is discrete (i.e., the bound states) and a part which is quantized. For some systems, some of the quantized states may be embedded in the energy continuum.

In most atomic and molecular non-BO calculations, e.g., calculations of rovibrational spectrum of a molecules, we are only interested in the bound states of the internal motion. Thus, it is convenient to separate out the operator representing the center-of-mass-motion from the total nonrelativistic laboratory-frame Hamiltonian. We have used two ways of performing this separation.

First let us consider an isolated atom or molecule consisting of N particles with masses  $\{M_i\}$  and charges  $\{Q_i\}$ . To write the laboratory-frame Hamiltonian, we use the lab-frame position vectors,  $\{\mathbf{R}_i\}$ , defining the positions of the particle relative to a space-fixed origin of the lab-frame coordinate system. The  $\{\mathbf{R}_i\}$  vectors are collected in the 3N dimensional vector  $\mathbf{R}$ .  $\mathbf{P}$  is the corresponding vector of the linear momenta of the particles:

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

With that, the lab-frame nonrelativistic Hamiltonian of the system is:

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

Next, the above Hamiltonian is separated into two independent Hamiltonians, the first representing the motion of the center of mass of the system and the second representing the internal motion of the particles forming the system. The dimensions of the two Hamiltonians are three and (3N - 3), respectively. The separation of the lab-frame Hamiltonian into the center-of-mass Hamiltonian and the internal Hamiltonian can be performed rigorously by expressing the lab-frame Hamiltonian in a new coordinate system whose first three coordinates are the Cartesian coordinates of

the center of mass,  $\mathbf{r}_0$ , in the laboratory coordinate frame and the remaining (3N-3) coordinates are the so-called internal coordinates. The internal coordinates, which are Cartesian, are denoted as  $\mathbf{r}_i$  (i = 1, ..., N - 1), where  $\mathbf{r}_i$  is the position vector of particle i + 1 with respect to particle 1 which is called the reference particle. Even though any particle in the system can be chosen as the reference particle, it usually the heaviest particle (nucleus). The obvious choice of the reference particle for an atom is its nucleus. The simplest case, where such a coordinate system has been used, is the textbook approach applied to solve the time-independent Schrödinger equation for the hydrogen atom. After the transformation of Hamiltonian (2) to be expressed in terms of the new coordinate system, it rigorously separates into the operator only dependent on  $\mathbf{r}_0$  representing the kinetic energy of the motion of the center of mass of the system,  $H_{nr}^{cm}(\mathbf{r}_0)$ , and the "internal" Hamiltonian, dependent on the (3N - 3) internal coordinates  $\mathbf{r}_i$  (i = 1, ..., N - 1) representing the internal motion,  $H_{nr}^{int}(\mathbf{r})$ :

$$H_{\rm nr}^{\rm tot}(\mathbf{r}_0, \mathbf{r}) = H_{\rm nr}^{\rm cm}(\mathbf{r}_0) + H_{\rm nr}^{\rm int}(\mathbf{r}), \qquad (3)$$

where **r** is a 3*n*-component column vector whose first three components are the coordinates of **r**<sub>1</sub>, the next three are the coordinates of **r**<sub>2</sub>, etc. A more detail form of  $H_{nr}^{tot}(\mathbf{r}_0, \mathbf{r})$  is:

$$H_{\rm nr}^{\rm tot}(\mathbf{r}_0, \mathbf{r}) = \left( -\frac{1}{2} \frac{1}{M_{\rm tot}} \nabla_{\mathbf{r}_0}^2 \right) \\ + \left( -\frac{1}{2} \sum_i^n \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 - \frac{1}{2} \sum_{i \neq j}^n \frac{1}{m_0} \nabla_{\mathbf{r}_i}' \nabla_{\mathbf{r}_j} + \sum_{i < j}^n \frac{q_i q_j}{r_{ij}} + \sum_{i=1}^n \frac{q_0 q_i}{r_i} \right), \quad (4)$$

where  $q_i = Q_{i+1}$  (i = 0, ..., n) are the charges of the particles,  $\mu_i = \frac{m_0 m_i}{m_0 + m_i}$  are their reduced masses,  $M_{\text{tot}}$  is the total mass of the system,  $m_0$  is the mass of the reference particle, and  $m_i = M_{i+1}$  are the masses of the particles.  $\nabla_{\mathbf{r}_i}$  is the gradient vector expressed in terms of the  $x_i, \gamma_i$ , 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  $r_{0i} \equiv r_i = |\mathbf{r}_i| = |\mathbf{R}_{i+1} - \mathbf{R}_1|$ . The prime symbol denotes the vector/matrix transposition.

The internal Hamiltonian is:

$$H_{\rm int}(\mathbf{r}) = \left( -\frac{1}{2} \sum_{i}^{n} \frac{1}{\mu_{i}} \nabla_{\mathbf{r}_{i}}^{2} - \frac{1}{2} \sum_{i \neq j}^{n} \frac{1}{m_{0}} \nabla_{\mathbf{r}_{i}}' \nabla_{\mathbf{r}_{j}} + \sum_{i < j}^{n} \frac{q_{i}q_{j}}{r_{ij}} + \sum_{i=1}^{n} \frac{q_{0}q_{i}}{r_{i}} \right).$$
(5)

As in most non-BO calculations one is only concerned with the internal bound states of the system, eigenvalues and eigenfunctions of the internal Hamiltonian are calculated.

The internal Hamiltonian,  $H_{int}(\mathbf{r})$ , describes a system of *n* pseudoparticles with the masses equal to reduced masses  $\mu_i$  and charges  $q_i$  (i = 1, ..., n) moving in the central field of the charge of the reference particle,  $q_0$ . We use the term "pseudoparticles" because, even though their charges are the same as the charges of the original particles, their masses are different. The motions of the pseudoparticles are coupled (correlated) through the Coulomb interactions and through the so-called mass-polarization terms,  $-\frac{1}{2}\sum_{i\neq j}^{n}\frac{1}{m_0}\nabla'_{\mathbf{r}_i}\nabla_{\mathbf{r}_j}$ . Hamiltonian (5) has the symmetry of an atomic Hamiltonian. Thus, as mentioned, its eigenfunctions are one-center functions that provide bases for irreducible representations of the SO(3) group of rotations. It should be noted that these symmetry properties equally apply to atoms and molecules regardless of the number of the nuclei.

Another way of separating out the center of mass motion from  $H_{nr}^{tot}(\mathbf{r}_0, \mathbf{r})$  is an effective way introduced some time ago by our group.<sup>20</sup> In the approach, instead of separating out the center-of-mass motion by introducing a new set of coordinates consisting of two subsets each describing a different type of motion, i.e., either the motion of the center of mass or the internal motion, the separation is done at the level of operators. Namely, we take the total Hamiltonian written in terms of the laboratory coordinates of all particles in the system,  $H_{nr}(\mathbf{R})$ , and subtract from it the Hamiltonian representing the kinetic energy of the center of mass motion. In this way, the Hamiltonian representing the internal motion is obtained:

$$H_{\rm int}(\mathbf{R}) = -\sum_{i=1}^{N} \frac{\mathbf{P}_{i}^{2}}{2M_{i}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_{i}Q_{j}}{|\mathbf{R}_{i} - \mathbf{R}_{j}|} - \frac{1}{2M_{\rm tot}} \mathbf{P}_{cm}^{2}$$
(6)

where  $\mathbf{P}_{cm}$  is the momentum operator associated with the motion of the center of mass.  $\mathbf{P}_{cm}$  is a sum of the operators representing the canonical momenta,  $\mathbf{p}(\mathbf{R}_i)$ , of all particles forming the system:

$$\mathbf{P}_{cm}(\mathbf{R}) = \sum_{i=1}^{N} \mathbf{p}(\mathbf{R}_i).$$
(7)

Note that, as the effective internal Hamiltonian,  $H_{int}(\mathbf{R})$ , depends on the laboratory coordinates of all particles forming the system, the wave function is also a function of all these coordinates. Thus, in the approach, the dimension

of the problem is not reduced by three, as happens in the first above-described approach. However, the effective internal Hamiltonian is also isotropic as is the internal Hamiltonian in the first approach. Thus, the calculations can be performed in a similar way using the two approaches.

We recently used the second approach to performed calculations of bound states of a molecule spatially confined by magnetic fields.<sup>21–23</sup> The wave functions in the calculations were expanded in terms of explicitly correlated Gaussian functions with shifted centers (see the next section). Two types of states of the molecule were considered in the calculations where the molecule was placed in a trap of rotating magnetic field with a constant strength.<sup>23</sup> The first type of states were internal bound states. They were calculated using the effective internal Hamiltonian of the second approach. The second type were translational and rotational states of the molecule within the trap. The calculations for those states were done using the full laboratory-frame Hamiltonian that included the interactions of the particles forming the molecule (i.e., the nuclei and the electrons) with the potential of the magnetic trap. The plots of the single-particle densities<sup>23</sup> enabled to elucidate the character of the states.

# 3. Basis functions used in atomic and molecular, ground and excited states non-BO calculations

The central issues in atomic and molecular non-BO calculations is selecting appropriate and effective basis functions for expanding the spatial part of the wave function. In this selection, the physical nature of the problem at hand needs to be considered and how this nature can be quantummechanically described with basis functions. In the BO quantum chemistry, there has been a lot of experience gathered concerning the coupled motion of the electrons around a stationary nucleus in an atom or around several stationary nuclei in a molecule. The key effects that have been considered for as long as quantum chemical calculations have been performed are the electron correlation effects. Even though these effects usually have a relatively small contribution to the total energy of the system, they play critical role in determining such atomic and molecular properties as spectral transitions, polarizabilities, intermolecular interaction energies, etc. The most popular way to account for the electron correlation effects in the electronic structure calculations is by expanding the wave functions in terms of a linear combination of Slater determinants constructed using a set of (usually mutually orthogonal) spin-orbitals. The linear coefficients multiplying the

determinants in the expansion can be determined either variationally (as it is done in the CI, MCSCF, CASSCF methods), perturbationally (as it is done in methods, like MPn, n = 1, ..., 4, based on the perturbation theory, or by solving a set of equations originating from projecting the Schrödinger equation on each determinant in the expansion (as it is done in the CCSD, CCSDT, CCSDTQ, ... methods). In some methods, the orbitals used to construct the determinants are also can be variationally optimized (as in CASSCF). Although not perfects, the methods based on orbital expansions are effective in performing electronic structure calculations even when the dynamic and nondynamic electron correlations effects are significant.

In non-BO calculations, the electron–electron (e–e) correlation effects are also important but two new types of correlations now come to play a role, the nucleus–nucleus (n–n) and nucleus–electron (n–e) correlations. The basis functions used in the calculation need to describe all three correlation types in addition to describing the radial and angular nodes that appear in the wave functions of excited states. For a set of particles interacting via a potential comprising pair-wise contributions (e.g., the Coulombic interactions) very effective basis functions for expanding the wave function of the system are functions that explicitly depend on the interparticle distances. Such functions, called explicitly correlated functions, have been adopted in quantum mechanical calculations of atomic and molecular systems within the BO approximation. Most commonly used are Gaussian explicitly correlated functions (ECGs).<sup>20,24–26</sup>

In non-BO calculations of ground and excited states of atoms and molecules we have used different forms of all-particle explicitly correlated Gaussians. For an atomic system with only *s*-electrons, the simplest ECG has the following one-center form:

$$\phi_{k} = \exp\left[-\alpha_{1k}r_{1}^{2} - \alpha_{2k}r_{2}^{2} - \dots - \alpha_{nk}r_{n}^{2} - \beta_{12,k}r_{12}^{2} - \beta_{13,k}r_{13}^{2} - \dots - \beta_{nn-1,k}r_{nn-1}^{2}\right],$$
(8)

where  $r_i$  is the distance between particle *i* and the center of the Gaussian, and  $\alpha_{ik}$  and  $\beta_{ij, k}$  and the nonlinear parameters of the Gaussian. This Gaussian can be represented in a more compact form as:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = \exp\left[-\mathbf{r}' \ \bar{\mathbf{A}}_{k} \ \mathbf{r}\right],\tag{9}$$

where  $\mathbf{A}_k$  is a  $3n \times 3n$  real symmetric matrix of exponential parameters.  $\mathbf{A}_k$  can be represented as:  $\mathbf{\bar{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$ , 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 be used as a basis function in expanding the wave function of a bound state of the system, function  $\phi_k(\mathbf{r})$  needs to be square-integrable. To ensure this, matrix  $\mathbf{A}_k$  must be positive definite. This automatically happens if  $\mathbf{A}_k$  is written in the Cholesky factored form as:  $\mathbf{A}_k = \mathbf{L}_k \mathbf{L}'_k$ , where  $\mathbf{L}_k$  is an  $n \times n$ , rank *n*, lower triangular matrix. If the matrix elements of  $\mathbf{L}_k$  are any real numbers,  $\phi_k(\mathbf{r})$  is automatically square-integrable. The matrix elements of  $\mathbf{L}_k$  are variationally optimized in our calculations. The energy gradient vector, which is used in the variational optimization, is determine with respect to these matrix elements.

In ECG basis functions for expanding the wave functions of states of the atom with one or more p, d, or f electrons, one needs to include angular preexponential factors.<sup>26,27</sup> In our works, we implemented basis functions where the ECG exponential are multiplied by Cartesian spherical harmonics. For P states of atoms with one p electron and other electrons being s electrons, the following Gaussians have been used:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = z_{i_{k}} \exp\left[-\mathbf{r}' \ \bar{\mathbf{A}}_{k} \ \mathbf{r}\right],\tag{10}$$

where index i varies from 1 to n and is also variationally optimized. For atomic D states the Gaussians are:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = (2z_{i_{k}}z_{j_{k}} - x_{i_{k}}x_{j_{k}} - \gamma_{i_{k}}\gamma_{j_{k}})\exp\left[-\mathbf{r}'\;\bar{\mathbf{A}}_{k}\;\mathbf{r}\right],\tag{11}$$

where indices  $i_k$  and  $j_k$  vary from 1 to n and they are variationally optimized in the calculations. We have also developed algorithms for performing ECG variational calculations for atomic F states with one f electron and other electron being s electrons<sup>27,28</sup> and algorithms for calculating states of atoms with two (carbon ground state) and three p electrons (nitrogen ground state).<sup>29,30</sup> In the nitrogen calculations the basis functions were:

$$\phi_{k}(\mathbf{r}) = \left[ (x_{j_{k}} \gamma_{i_{k}} - x_{i_{k}} \gamma_{j_{k}}) z_{k_{k}} + (x_{i_{k}} \gamma_{k_{k}} - x_{i_{k}} \gamma_{i_{k}}) z_{j_{k}} + (x_{i_{k}} \gamma_{j_{k}} - x_{j_{k}} \gamma_{k_{k}}) z_{i_{k}} \right] \exp\left[ -\mathbf{r}' \ \bar{\mathbf{A}}_{k} \ \mathbf{r} \right],$$
(12)

where indices  $i_k$ ,  $j_k$ , and  $k_k$  were variationally optimized along with the matrix elements of  $L_k$ .

For molecules, the non-BO wave functions need to describe a complicated physical situation due to the nuclear–nuclear correlation effects coming to play. For the electrons, which are light particles, their wave functions overlap to significant extent. When this happens, the dependency of the basis functions on the interparticle distances only in the Gaussian exponential factors is quite sufficient to describe the e–e correlation effects. However, as the probability of finding two nuclei at the same spatial point is much smaller than for the electrons due to their heavier masses, additional correlation factors need to be included in the explicitly correlated Gaussians used to expand the wave function in non-BO calculations. One needs such factors because at coalescent points  $(r_{ij} \rightarrow 0)$  the Gaussians with interparticle distances in the exponent have maxima, which are desirable to describe the n-e correlation, but not desirable in describing the n-n correlation. Different preexponential factors can be chosen for ECGs to better describe the n-n correlation, but, in general, these factors should significantly lower the probability of finding two nuclei at the same point of space (or even make the probability to go to zero). This effect can be most effectively achieved by making the factors dependent on the internuclear distances. Note, that using the orbital approach, which is a fairly accurate approach for electrons, to perform a non-BO molecular calculation would give inaccurate results, as the n-n correlation is very strong. The factors should also be capable of describing radial oscillations (and nodes) of the wave functions for vibrationally excited states. The nodes in these wave functions appear in terms of internuclear distances. It should be noted that the angular nodes in the wave functions are described by Cartesian spherical harmonics.

About two decades ago we showed<sup>31–34</sup> that, in the case of diatomic molecule, effective preexponential correlation factors for ECGs are nonnegative power of the internuclear distance and for molecules with more than two nuclei the factors are products of nonnegative powers of all intermolecular distances. We call the Gaussians with such multipliers "power Gaussians". For a diatomic system the power Gaussian used in expanding wave functions of diatomic in states with rotational quantum number of zero has the following form:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = r_{1}^{2p_{k}} \exp\left[-\mathbf{r}' \ \bar{\mathbf{A}}_{k} \ \mathbf{r}\right], \tag{13}$$

where  $r_1$  is the distance between the reference nuclei and particle *i*, which is usually chosen to be the second nucleus.  $2p_k$  is the integer nonnegative power of  $r_1$  (ranging from 0 to 250) in our calculations; we only use even powers as this considerably simplifies the calculation of the Hamiltonian integrals; using only even powers has almost no effect on the accuracy of the calculation).

When the  $2p_k$  power value at fixed  $\mathbf{A}_k$  in (13) increases, the average distance between the two nuclei also increases. Gaussians with the zero value of  $2p_k$  need to be included in the basis set to account for residual probability of finding both nuclei in the same point in space. The  $2p_k$  power is variationally optimized in the calculation. The other purpose of including the  $r_1^{2p_k}$  multipliers in the Gaussians, is, as mentioned, to describe the wave-function oscillations (nodes) due to vibrational excitations. The multipliers are very effective in performing this task.

For a triatomic molecule the power Gaussian has the following form<sup>35</sup>:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = r_{1}^{2p_{k}^{(1)}} r_{2}^{2p_{k}^{(2)}} r_{12}^{2p_{k}^{(12)}} \exp\left[-\mathbf{r}' \ \bar{\mathbf{A}}_{k} \ \mathbf{r}\right], \tag{14}$$

where  $r_1$ ,  $r_2$ , and  $r_{12}$  are internuclear distances and  $2p_k^{(1)}$ ,  $2p_k^{(2)}$ , and  $2p_k^{(12)}$  are their respective nonnegative even-integer powers. We should mention that we encountered some difficulties in the implementation of basis functions (14).<sup>35</sup> They originated from numerical instabilities and divergence of the algorithms for calculating Hamiltonian matrix elements with these functions.

Basis functions (13) has been implemented and used to perform calculations of rotation-less vibrational spectra of diatomic molecules.<sup>36</sup> We also implemented the following power Gaussians for expanding the wave functions of diatomic states corresponding to the rotational quantum number of one<sup>37</sup>:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = z_{i_{k}} r_{1}^{2p_{k}} \exp\left[-\mathbf{r}' \ \bar{\mathbf{A}}_{k} \ \mathbf{r}\right], \tag{15}$$

where the particle index  $i_k$  is a variational parameter. An interesting aspect of using Gaussians (15) in calculating rovibrational states with L = 1 for diatomic is related the values of i that come out from the calculation. As the second nucleus is the number one pseudoparticle in the internal Hamiltonian and pesudoparticles 2, 3, ..., n are the electrons, one would expect that the non-BO wave functions corresponding to the first rotational excitation to be primarily formed by basis functions with index *i* of one. This type of basis functions represent the L = 1 angular excitation of the nuclei. This indeed happens, but there also are nonnegligible contributions from basis functions with i's not equal to one. The contributions of these functions, which represent angular excitations of the electrons, increase with the vibrational excitation. This shows that there is some coupling between angular excitations of the nuclei (i.e., the conventional rotational excitations) and angular excitations of the electrons (i.e., some basis functions representing  $\Pi$  excited electronic states mix in with basis functions representing L = 1 angular excitations of the nuclear motion).

Amidst the inability of extending the power Gaussian approach to triatomics we have been searching for other forms of preexponential multipliers that would produce a similar behavior of the wave function as products of powers of internuclear distances. One possibility that came to mind was to use products of *sin* and *cos* functions of the internuclear distances multiplied by variational parameters (or *sin* and *cos* functions of squares of the internuclear distances). However, as the *sin* and *cos* functions can be expressed in terms of complex exponentials, one can construct basis functions for non-BO atomic and molecular calculations as products of these complex exponentials and the Gaussian exponents.

This is the approach we have been developing and testing in recent years as an alternative form of ECGs for molecular non-BO calculations.<sup>38–40</sup> These alternative basis functions are all-particle explicitly correlated Gaussians with complex exponential parameters (complex ECGs or CECGs, for short). For expanding the wave functions of states corresponding to the total-rotational quantum number of zero we use the following complex Gaussians<sup>38</sup>:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = \exp\left[-\mathbf{r}' \ \bar{\mathbf{C}}_{k} \ \mathbf{r}\right] = \exp\left[-\mathbf{r}' \ (\bar{\mathbf{A}}_{k} + \mathrm{i}\bar{\mathbf{B}}_{k}) \ \mathbf{r}\right], \tag{16}$$

where  $\bar{\mathbf{A}}_k$ , as in (9), is a real symmetric positive-definite matrix,  $\bar{\mathbf{B}}_k$  is a real symmetric matrix, and  $i = \sqrt{-1}$ . The matrix elements of both matrices are variational parameters that are optimized in the calculation.  $\bar{\mathbf{A}}_k$  and  $\bar{\mathbf{B}}_k$  can be written as:  $\bar{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$  and  $\bar{\mathbf{B}}_k = \mathbf{B}_k \otimes \mathbf{I}_3$ . For L = 1 ( $M_L = 0$ ) states the CECGs are<sup>40</sup>:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = z_{i_{k}} \exp\left[-\mathbf{r}' \ \bar{\mathbf{C}}_{k} \ \mathbf{r}\right] = z_{i_{k}} \exp\left[-\mathbf{r}' \ \left(\bar{\mathbf{A}}_{k} + \mathrm{i}\bar{\mathbf{B}}_{k}\right) \mathbf{r}\right], \tag{17}$$

where  $z_{i_k}$ , as before, is the *z* internal coordinate of particle  $i_k$ . Index  $i_k$  is also variationally optimized. For L = 2 ( $M_L = 0$ ) states the CECGs are:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = (2z_{i_{k}}z_{j_{k}} - x_{i_{k}}x_{j_{k}} - \gamma_{i_{k}}\gamma_{j_{k}}) \exp\left[-\mathbf{r}' \ \bar{\mathbf{C}}_{k} \ \mathbf{r}\right]$$

$$= \exp\left[-\mathbf{r}' \ (\bar{\mathbf{A}}_{k} + \mathrm{i}\bar{\mathbf{B}}_{k}) \ \mathbf{r}\right].$$
(18)

It should be noted that the above-defined CECGs are equally well suited to perform atomic and molecular non-BO calculations. Thus, a single computer code is used for both types of calculations. The development of the CECG approach is an active project in our research group.

Finally, there are the ECGs with shifted centers. The functions have the following form:

$$\boldsymbol{\phi}_{k}(\mathbf{r}) = \exp\left[-(\mathbf{r} - \mathbf{s}_{k})' \,\bar{\mathbf{A}}_{k} \,(\mathbf{r} - \mathbf{s}_{k})\right],\tag{19}$$

where  $\mathbf{s}_k$  is a vector of the Gaussian shifts, whose coordinates are variational parameters which are optimized in the calculation, and  $\mathbf{\bar{A}}_k$  is a symmetric positive-definite matrix of exponential variational parameters. We have developed and implemented algorithms for calculating Hamiltonian and overlap matrix elements, as well as the matrix elements of the energy gradient vector determined with respect to the variational parameters.<sup>19,41–46</sup> The ECGs with shifted centers were employed in non-BO calculations of the dipole moments of isotopologues of H<sub>2</sub> and LiH<sup>43,45</sup> and in non-BO calculations of molecules placed in magnetic traps.<sup>21–23</sup> They were also used in the non-BO calculations of isotopologues of H<sub>3</sub>.<sup>19</sup> The project concerning non-BO calculations of molecules trapped in molecular clathrates and of molecules in magnetic traps is active in our research group.

# 4. Numerical example

One of the main results that can be obtained from non-BO calculations are isotopic shifts of the transition energies. As the variational ECG calculations are performed for different nuclear masses, slightly different transition energies are obtained for different isotopes. For an atom, the difference between a transition energy calculated at the non-BO nonrelativistic level of theory using an infinite nuclear mass and the transition energy calculated for a particular isotope accounts for the sum of so-called adiabatic and nonadiabatic corrections. In conventional calculations, one usually employs the perturbation theory to account for these corrections.<sup>47</sup> The value of the isotopic energy shift we obtain in our calculations is equivalent to accounting for the adiabatic and nonadiabatic corrections to infinite order of the perturbation theory.

To illustrate how isotopic shifts of transition energies are calculated for an atomic system, we perform calculations in this work of ten lowest singlet states of each of the *S*, *P*, and *D* symmetries for the helium atom. The basis set for each *S* state is grown to the size 2000 Gaussians by starting with small a number of functions obtained using an orbital approximation for the lowest state and then gradually increasing the number of functions by adding sets of 10–20 Gaussians and optimizing them using the gradient-aided variational energy minimization subroutine. After each addition of a set of 10–20 Gaussians the whole basis set is reoptimized. The basis sets are generated for  $^{\infty}$ He. The energies obtained in the calculations with 2000 basis functions are shown in Table 1 and compared with the  $^{\infty}$ He energies calculated by Drake with Hylleraas-type explicitly correlated functions.<sup>48</sup> As the Hylleraas functions are better than the Gaussians because they have proper

Isotope	State	Basis	Energy	State	Basis	Energy
<sup>3</sup> He	$1^1S$	2000	-2.903 167 210 711 60	$2^1S$	2000	-2.145 581 923 703 81
<sup>4</sup> He		2000	-2.903 304 557 729 85		2000	-2.145 678 587 580 72
∞He		2000	-2.903 724 377 034 11		2000	-2.145 974 046 054 37
∞He		2000	-2.903 724 377 034 119(5)		Ref. 48	-2.145 974 046 054 419(6)
<sup>3</sup> He	$3^1S$	2000	-2.060 896 524 124 36	$4^1S$	2000	-2.033 216 570 275 63
<sup>4</sup> He		2000	-2.06098908234911		2000	-2.033 307 817 481 22
∞He		2000	-2.06127198974082		2000	-2.033 586 717 030 53
∞He		Ref. 48	-2.061 271 989 740 911(5)		Ref. 48	-2.033 586 717 030 72(1)
<sup>3</sup> He	$5^1S$	2000	-2.02080905931457	$6^1S$	2000	-2.014 196 551 201 72
<sup>4</sup> He		2000	-2.020 899 726 173 69		2000	-2.014 286 911 184 33
∞He		2000	-2.021 176 851 574 35		2000	-2.014 563 098 446 43
∞He		Ref. 48	-2.021 176 851 574 363(5)		Ref. 48	-2.014 563 098 446 60(1)
<sup>3</sup> He	$7^1S$	2000	-2.01025996617961	$8^1S$	2000	-2.007 728 284 333 27
<sup>4</sup> He		2000	-2.010 350 144 450 84		2000	-2.007 818 346 200 10
∞He		2000	-2.01062577621019		2000	-2.008 093 622 103 36
∞He		Ref. 48	-2.010 625 776 210 87(2)		Ref. 48	-2.008 093 622 105 61(4)
<sup>3</sup> He	$9^1S$	2000	-2.00600453589712	$10^1 S$	2000	-2.004 778 202 005 56
<sup>4</sup> He		2000	-2.00609451874984		2000	-2.004 868 128 777 66
∞He		2000	-2.00636955309063		2000	-2.005 142 991 666 85
∞He		Ref. 48	-2.006 369 553 107 85(3)		Ref. 48	-2.005 142 991 748 00(8)
<sup>3</sup> He	$2^1 P$	2000	-2.12344834501821	$3^1 P$	2000	-2.054 769 843 455 48
<sup>4</sup> He		2000	-2.12354565412741		2000	-2.054 862 661 148 41
∞He		2000	-2.12384308649808		2000	-2.055 146 362 091 91
∞He		Ref. 48	-2.123 843 086 498 093(2)		Ref. 48	-2.055 146 362 091 94(3)
<sup>3</sup> He	$4^1 P$	2000	-2.030 699 019 274 66	$5^1P$	2000	-2.019 537 939 377 19

**Table 1** Convergence of the total energies of *S*, *P*, and *D* states of <sup>3</sup>He, <sup>4</sup>He, and <sup> $\infty$ </sup>He with the number of ECGs.

lsotope	State	Basis	Energy	State	Basis	Energy
<sup>4</sup> He		2000	-2.03079038585043		2000	-2.019 628 669 880 63
∞He		2000	-2.03106965045021		2000	-2.019 905 989 900 82
∞He		Ref. 48	-2.031 069 650 450 24(3)		Ref. 48	-2.016 905 989 900 83(2)
<sup>3</sup> He	$6^1 P$	2000	-2.013 467 279 455 70	$7^1P$	2000	-2.009 803 406 706 90
<sup>4</sup> He		2000	-2.01355767713581		2000	-2.009 893 609 078 17
∞He		2000	-2.01383397967171		2000	-2.010 169 314 529 25
∞He		Ref. 48	-2.013 833 979 671 73(2)		Ref. 48	-2.010 169 314 529 35(2)
<sup>3</sup> He	$8^1 P$	2000	-2.007 423 723 160 05	$9^1 P$	2000	-2.005 791 320 599 70
<sup>4</sup> He		2000	-2.007 513 801 342 14		2000	-2.005 881 314 995 65
∞He		2000	-2.007 789 127 132 75		2000	-2.006 156 384 639 40
∞He		Ref. 48	-2.007 789 127 133 22(2)		Ref. 48	-2.006 156 384 652 86(5)
<sup>3</sup> He	$10^1 P$	2000	-2.00462315955120	$11^1 P$	2000	-2.003 758 543 164 83
<sup>4</sup> He		2000	-2.004 713 094 792 39		2000	-2.003 848 435 093 31
∞He		2000	-2.00498798357547		2000	-2.004 123 191 461 86
∞He		Ref. 48	-2.004 987 983 802 22(4)			
<sup>3</sup> He	$3^1D$	1600	-2.05524681910431	$4^1D$	1600	-2.030 910 337 853 95
<sup>4</sup> He		1600	-2.05533899479363		1600	-2.031 001 427 686 13
∞He		1600	-2.05562073285209		1600	-2.031 279 846 178 51
∞He		Ref. 48	-2.055 620 732 852 246(6)		Ref. 48	-2.031 279 846 178 687(7)
<sup>3</sup> He	$5^1D$	2000	-2.019 648 362 990 92	$6^1D$	2000	-2.013 531 864 960 64
<sup>4</sup> He		2000	-2.019 738 952 225 18		2000	-2.013 622 179 400 54
∞He		2000	-2.02001583250975		2000	-2.013 898 227 424 13
∞He		Ref. 48	-2.020 015 836 159 984(4)		Ref. 48	-2.013 898 227 424 286(5)
<sup>3</sup> He	$7^1D$	2000	-2.009 844 334 034 71	$8^1D$	2000	-2.007 451 251 857 90
<sup>4</sup> He		2000	-2.009 934 483 813 42		2000	-2.007 541 294 732 41
						Continued

**Table 1** Convergence of the total energies of *S*, *P*, and *D* states of <sup>3</sup>He, <sup>4</sup>He, and <sup> $\infty$ </sup>He with the number of ECGs.—cont'd

lsotope	State	Basis	Energy	State	Basis	Energy
∞He		2000	-2.01021002845614		2000	-2.007 816 512 559 50
∞He		Ref. 48	-2.010 210 028 457 98(1)		Ref. 48	-2.007 816 512 563 811(7)
<sup>3</sup> He	$9^1D$	2100	-2.005 810 708 148 99	$10^1 D$	2200	-2.004 637 320 667 84
<sup>4</sup> He		2100	-2.00590067771297		2200	-2.004 727 237 837 91
∞He		2100	-2.00617567141639		2200	-2.005 002 071 264 43
∞He		Ref. 48	-2.006 175 671 437 641(6)		Ref. 48	-2.005 002 071 654 250(6)
<sup>3</sup> He	$11^{1}D$	2300	-2.00376919803009	$12^1D$	2300	-2.003 108 951 617 70
<sup>4</sup> He		2300	-2.00385907642347		2300	-2.003 198 800 508 45
∞He		2300	-2.004 133 791 233 01		2300	-2.003 473 425 087 32

**Table 1** Convergence of the total energies of *S*, *P*, and *D* states of <sup>3</sup>He, <sup>4</sup>He, and <sup> $\infty$ </sup>He with the number of ECGs.—cont'd

All values are given in a.u.

asymptotic behavior, it takes more Gaussians to match the results obtained with the Hylleraas-type functions. The same procedure is used to generate basis set for the ten lowest P states and ten lowest D states. Note that a couple of top P and D states were not calculated by Drake.

The present ECG results for <sup> $\infty$ </sup>He are in very good agreement with Drake's energies. The agreement is particularly good for lower states where almost all 15 digits shown by Drake are reproduced by the present calculations. For top states the agreement is somewhat lower, but still 10–11 digits are reproduced. The basis sets for all considered states obtained from the optimizations performed for <sup> $\infty$ </sup>He are used in the calculations for <sup>3</sup>He and <sup>4</sup>He, and the results are also shown in Table 1. So, only the linear expansion coefficients in the wave functions are adjusted when going from <sup> $\infty$ </sup>He to <sup>4</sup>He and to <sup>3</sup>He. Our previous experience indicates that this suffices for obtaining quite accurate values of the isotopic energy shifts.

Next, the energies obtained for the *S*, *P*, and *D* states of <sup>3</sup>He, <sup>4</sup>He, and <sup> $\infty$ </sup>He are used to calculate transition energies relative to the lowest state of the particular symmetry for the given isotope. The results are shown in Table 2. The values shown for <sup> $\infty$ </sup>He are the whole transition energies, but the values shown for <sup>3</sup>He and <sup>4</sup>He are differences between the transition energies for the particular states of the particular isotopes and the corresponding values for <sup> $\infty$ </sup>He. Thus, the values shown in columns marked as <sup>3</sup>He and <sup>4</sup>He are the isotopic shifts, i.e., the sums of the adiabatic and nonadiabatic corrections.

	S			Р				D			
Transition	∞He	⁴He	<sup>3</sup> He	Transition	<sup>∞</sup> He	⁴He	<sup>3</sup> He	Transition	<sup>∞</sup> He	⁴He	<sup>3</sup> He
$2^1 S \rightarrow 1^1 S$	166 306.951	-27.294	-36.223	$3^1 P \rightarrow 2^1 P$	150 77.186	-3.014	-3.999	$4^1D \rightarrow 3^1D$	534 2.206	-0.729	-0.967
$3^1S \rightarrow 1^1S$	184 896.901	-30.049	-39.879	$4^1 P \rightarrow 2^1 P$	203 61.413	-3.987	-5.292	$5^1D \rightarrow 3^1D$	781 4.371	-1.066	-1.414
$4^1 S \rightarrow 1^1 S$	190 973.115	-30.928	-41.046	$5^1 P \rightarrow 2^1 P$	228 11.553	-4.414	-5.858	$6^1 D \rightarrow 3^1 D$	915 7.030	-1.249	-1.657
$5^1 S \rightarrow 1^1 S$	193 696.765	-31.318	-41.563	$6^1 P \rightarrow 2^1 P$	241 44.205	-4.637	-6.154	$7^1D \rightarrow 3^1D$	996 6.496	-1.359	-1.804
$6^1 S \rightarrow 1^1 S$	195 148.316	-31.524	-41.836	$7^1 P \rightarrow 2^1 P$	249 48.506	-4.769	-6.328	$8^1D \rightarrow 3^1D$	104 91.812	-1.431	-1.899
$7^1S \rightarrow 1^1S$	196 012.458	-31.646	-41.998	$8^1 P \rightarrow 2^1 P$	254 70.896	-4.852	-6.439	$9^1D \rightarrow 3^1D$	108 51.935	-1.480	-1.964
$8^1 S \rightarrow 1^1 S$	196 568.202	-31.724	-42.101	$9^1 P \rightarrow 2^1 P$	258 29.242	-4.908	-6.513	$10^1 D \rightarrow 3^1 D$	111 09.511	-1.515	-2.011
$9^1S \rightarrow 1^1S$	196 946.591	-31.777	-42.172	$10^1 P \rightarrow 2^1 P$	260 85.676	-4.948	-6.566	$11^1D \rightarrow 3^1D$	113 00.076	-1.541	-2.046
$10^1 S \to 1^1 S$	197 215.790	-31.814	-42.222	$11^1 P \rightarrow 2^1 P$	262 75.476	-4.977	-6.605	$12^1D \rightarrow 3^1D$	114 45.010	-1.561	-2.072

**Table 2** Transition energies of *S*, *P*, and *D* states of <sup>3</sup>He, <sup>4</sup>He, and <sup> $\infty$ </sup>He with respect to the lowest state of the particular symmetry.

For  ${}^{\infty}$ He the whole transition energy is given. For  ${}^{3}$ He and  ${}^{4}$ He the differences with respect to the transition energy of  ${}^{\infty}$ He are shown, for example, to get the transition energy of  ${}^{3}$ He the value shown in the  ${}^{3}$ He column should be added to the  ${}^{\infty}$ He transition energy. All values are given in cm<sup>-1</sup>.

An analysis of the results shown in Table 2 shows that the the mass effect is quite significant, particularly for the S states. The transition energy for the lowest S state,  $2^{1}$ S, shifts by -27.294 cm<sup>-1</sup> from <sup>∞</sup>He to <sup>4</sup>He and by -36.223 cm<sup>-1</sup> from <sup>∞</sup>He to <sup>3</sup>He. So, this transition frequency shifts by -8.929 cm<sup>-1</sup> in going from <sup>4</sup>He to <sup>3</sup>He. The other S-state transitions shift by similar amounts. The transition for the top  $10^1S$  state shifts by -31.814 cm<sup>-1</sup> for <sup>4</sup>He and by -42.222 cm<sup>-1</sup> for <sup>3</sup>He. So, the transition for  ${}^{3}$ He is shifted with respect to the transition for  ${}^{4}$ He by 10.408 cm<sup>-1</sup>. For the P states, the transition energy shifts are smaller and range from -3.014 cm<sup>-1</sup> for the lowest excited P state of <sup>4</sup>He to -4.977 cm<sup>-1</sup> for the top state. For <sup>3</sup>He the values are -3.999 cm<sup>-1</sup> and -6.605 cm<sup>-1</sup>, respectively. So, from <sup>4</sup>He to <sup>3</sup>He the lowest *P* transition shifts by -0.985 cm<sup>-1</sup> and the highest P transition shifts by -1.628 cm<sup>-1</sup>. For the D states the shifts are even smaller and for <sup>4</sup>He they are -0.729 cm<sup>-1</sup> and -1.561 cm<sup>-1</sup> for the bottom and top states, respectively, and for  ${}^{3}$ He they are -0.967 and -2.072 cm<sup>-1</sup>, respectively. So, from <sup>4</sup>He to <sup>3</sup>He the lowest D transition shifts by  $-0.238 \text{ cm}^{-1}$  and the highest D transition shifts by  $-0.511 \text{ cm}^{-1}$ .

Even though the Hylleraas functions give better results for higher states, as shown in Table 1, the difference can be reduced if more Gaussians are included in the basis set. Obviously, the number of ECGs of 2000 which gives very good results for the lowest states cannot be expected to produce results of the same quality for the top states. Also, it should be mentioned that, while the use of the Hylleraas functions is limited to atomic systems with up to three electrons, the use of ECGs is only limited by the available computational resources. We should note that the timing for the variational ECG atomic calculation scales as the factorial of the number of electrons in the system. This makes the calculations for the carbon and nitrogen atoms much more time consuming than the calculations for helium.

### 5. Perspectives

There is number of directions the ECG techniques can be developed and applied in future research. Let us mention a few of these directions that can evolve from the work described in this review.

 We see a big potential in the all-particle complex explicitly correlated Gaussian functions to calculate ground and excited states of first- and second-row atoms. By incorporating Cartesian spherical harmonics in these functions, calculations for atomic spectra can be performed with high accuracy. We have already implemented the algorithms for calculating the leading relativistic corrections for the *S* states. Extending these calculations for states with higher angular momenta is forthcoming. Also, an approach to calculate the fine and hyperfine atomic splitting has been implemented for real Gaussians and will be soon extended to the complex Gaussians. With that extension, the calculation of the fine and hyperfine splitting will become possible for higher-angular-momenta atomic states. The complex-Gaussian approach will also be applied in non-BO calculations of rovibrational spectra of small molecules. As the same computer code is used in both atomic and molecular calculations, the properties calculated for atoms (e.g., fine and hyperfine splitting) can also be calculated for molecules. Particularly interesting will be non-BO calculations of rovibrational spectra of the  $H_3^+$  ion and its isotopologues.

- 2. An interesting problem to study is bound states of atoms and molecules spatially confined by optical and magnetic traps, or confined to cages formed by molecular networks. The non-BO approach and the explicitly correlated Gaussians with shifted centers are very well suited to calculate such states, which can be either internal states, or translational/rotational states, or have characteristics of both types of states. The study of confined molecules is related, for example, to storing hydrogen gas in molecular cages as fuel. The study of confined atoms is related, for example, to use of single Rydberg atoms as so-called qubits in quantum computers. Another example is the behavior of small molecular systems in interstellar space trapped by quickly rotating, very strong magnetic fields. Molecular phenomena related to the interaction with very strong magnetic fields cannot be studied in the laboratory because such magnetic field strengths are not attainable on earth.
- **3.** With the advent of ultrashort, intense laser pulses capable of probing electronic processes with high resolution in both space and time, there is a demand for highly accurate simulations of many-electron dynamics. As the fast motion of the electrons and slower motion of the nuclei couple in these processes, an adequate dynamical model has to enable to treat electrons and nuclei on an equal footing. The approach based on using ECGs described in this review, especially the methods employing the effective internal Hamiltonian and explicitly correlated Gaussians with shifted centers seem promising to be applied to study the electronic-nuclear molecular dynamics.

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