

A non-Born–Oppenheimer self-consistent field method

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This communication outlines the development of a novel method for the *ab initio* computation of molecular systems wherein the Born–Oppenheimer approximation is not invoked. In the current method, a common Hamiltonian is employed to operate on the electrons and nuclei simultaneously. In addition, an inseparable wavefunction is generated to describe the non-Born–Oppenheimer behaviour. The physical implications of the new method are discussed.

KEY WORDS: Born–Oppenheimer approximation, self-consistent field, nuclear wavefunction

1. Introduction

The Born–Oppenheimer approximation is one of the cornerstones upon which modern quantum chemistry is founded. The application of this approximation has made it possible to treat systems containing more than a small number of particles (nuclei and electrons). However, it must be recalled that the BO method is still an approximation. The Born–Oppenheimer approximation is a technique that implicitly assumes the separability of nuclear and electronic motion in a bound system. The method treats electronic and nuclear motion independently, the only interaction between the two realms being through the electrostatic potential term [1,2]. Under the adiabatic approximation, the molecular wavefunction is approximated as the product of electronic and nuclear wavefunctions.

$$\Psi = \psi_e \psi_n. \quad (1)$$

A method based on implementation of the nuclear delocalisation has been introduced by Thomas [3–10] and implemented by Bochevarov et al. in the

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ENMO (electrons and nuclei molecular orbital) method [11]. However, the ENMO method also suffers from the issue of separability.

The purpose of this study is to explore ways in which the separability approximation can be removed. Removal of the separability approximation would allow the accurate calculation of the electron density distribution in a molecule. The inability to compute the density distribution accurately currently precludes the ability to compute electronic spectra to high accuracy, for example using time-dependent methods [12]. This is further illustrated by the fact that Born–Oppenheimer calculations are unable to reproduce the difference in electronic excitation energies that have been observed in small molecules [13]. In addition, there are systems for which the “fixed nuclei” model yields inadequate results, such as the cooperative electron-proton transfer (CEPT) reactions observed in biological systems [14]. Previous efforts at transcending the Born–Oppenheimer approximation have traditionally taken two approaches (a) treating nuclear motion as a perturbation [15–18], or (b) solving the molecular wavefunction for electrons and nuclei in a self-consistent manner [3–11,19–26]. This study combines the motivations of the second approach with the methods developed in the former.

The general non-Born–Oppenheimer wavefunction is given by Handy et al. [15] and others [17] to be

$$\Psi = \sum_i \psi_{ni}(R) \psi_{ei}(r, R), \quad (2)$$

where the coordinates R and r refer to the nuclear and electronic coordinates and the index i runs over a series of unspecified pairs of nuclear and electronic wavefunctions. It can be directly seen that the above wavefunction is non-separable into the electronic and nuclear wavefunctions.

2. Method

It has been stated that “One of the most urgent problems of modern quantum chemistry is to treat the motions of the atomic nuclei and the electrons on a more or less equivalent basis” [27]. This is also preferable as the treatment of nuclei as quantum particles is necessary for the proper physical representation of the system. Hence, there is importance in generating a method that treats the nuclei equivalently as quantum particles. The generalized Hamiltonian is given by

$$\hat{H} = \sum_i -\frac{1}{2m_i} \nabla_i^2 + \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}}, \quad (3)$$

where the summation runs over all particles in the system. This ensures that the electrons and nuclei are treated in an equivalent fashion, as there is no

distinction made in the Hamiltonian as to whether the particles in question are nuclei or electrons.

To be a true non-Born–Oppenheimer method, the wavefunction should be inseparable between electronic and nuclear contributions. The wavefunction is required to be anti-symmetric with respect to interchange of identical fermions, and symmetric with respect to interchange of bosons [28]; the wavefunction of non-identical particles is also symmetric with respect to interchange [29]. A completely coupled wavefunction satisfying the above conditions can be constructed by

$$\Psi = \frac{1}{\sqrt{N}} \sum_i \left[S_i \prod_{n=1}^{\text{fermions}} |\mathbf{D}_i^n| \prod_{n=1}^{\text{bosons}} |\mathbf{D}_i^n|_+ \right], \tag{4}$$

wherein the interchange is permitted between particles of both types. The requirements of exchange symmetry lead to a situation wherein the electrons can occupy nucleus-like orbitals and *vice versa*. This permits a better description of the electron density near the mean position of the nucleus. Additionally, permitting nuclei to occupy electronic orbitals lends some flexibility in their positional distributions. The probability of interchange between two particles is a function of the overlap between the wavefunctions housing the two particles [29]. Hence, the various terms in Ψ are scaled by the overlap integrals S_i .

$$S_i = \prod_{n=1}^k \langle |\mathbf{D}_0^n| \mid |\mathbf{D}_i^n| \rangle. \tag{5}$$

In the above relation, $|\mathbf{D}_i^n|$ refers to the determinant of particle type n in the i th term of the expansion. The $|\mathbf{D}_0^n|$ refers to the first (‘reference’) term in the expansion. For example, the wavefunction for the H_2 molecule is given by

$$\Psi = \frac{1}{\sqrt{N}} \left[\begin{array}{l} \left| \begin{array}{cc} \psi_1(r_1) & \psi_2(r_1) \\ \psi_1(r_2) & \psi_2(r_2) \end{array} \right| \left| \begin{array}{cc} \psi_3(r_3) & \psi_4(r_3) \\ \psi_3(r_4) & \psi_4(r_4) \end{array} \right| + S_{13} \left| \begin{array}{cc} \psi_3(r_1) & \psi_2(r_1) \\ \psi_3(r_2) & \psi_2(r_2) \end{array} \right| \left| \begin{array}{cc} \psi_1(r_3) & \psi_4(r_3) \\ \psi_1(r_4) & \psi_4(r_4) \end{array} \right| \\ + S_{14} \left| \begin{array}{cc} \psi_4(r_1) & \psi_2(r_1) \\ \psi_4(r_2) & \psi_2(r_2) \end{array} \right| \left| \begin{array}{cc} \psi_3(r_3) & \psi_1(r_3) \\ \psi_3(r_4) & \psi_1(r_4) \end{array} \right| + S_{23} \left| \begin{array}{cc} \psi_1(r_1) & \psi_3(r_1) \\ \psi_1(r_2) & \psi_3(r_2) \end{array} \right| \left| \begin{array}{cc} \psi_2(r_3) & \psi_4(r_3) \\ \psi_2(r_4) & \psi_4(r_4) \end{array} \right| \\ + S_{24} \left| \begin{array}{cc} \psi_1(r_1) & \psi_4(r_1) \\ \psi_1(r_2) & \psi_4(r_2) \end{array} \right| \left| \begin{array}{cc} \psi_3(r_3) & \psi_2(r_3) \\ \psi_3(r_4) & \psi_2(r_4) \end{array} \right| + S_{13}S_{24} \left| \begin{array}{cc} \psi_3(r_1) & \psi_4(r_1) \\ \psi_3(r_2) & \psi_4(r_2) \end{array} \right| \left| \begin{array}{cc} \psi_1(r_3) & \psi_2(r_3) \\ \psi_1(r_4) & \psi_2(r_4) \end{array} \right| \end{array} \right], \tag{6}$$

where particles 1 and 2 are particles of one type (say electrons) and particles 3 and 4 are of the other type (protons), and the ψ s refer to occupied wavefunctions. The maximum number of terms in the wavefunction expansion for a system of K particles of k distinguishable types, where there are n_i particles of type i (i is contained in k) is given by

$$NT = \prod_{i=1}^{k-1} \frac{(K - \sum_{p=1}^{i-1} n_p)!}{n_i!(K - \sum_{p=1}^i n_p)!} \tag{7}$$

where the summation is over all particle types (k) and all particles (K) are included in the combinatorial expansion. Notably, there are now no zero terms in the expansion as the interchange has been constrained to only the spatial parts of the spin orbitals. The total number of Fock equations to be solved then becomes

$$NE = \left(\prod_{i=1}^{k-1} \frac{(K - \sum_{p=1}^{i-1} n_p)!}{n_i! (K - \sum_{p=1}^i n_p)!} \right)^2 \quad (8)$$

This is then an upper bound that is only attained in the (unlikely) situation that there are identical numbers of particles of each particle type in the system. The normalization factor N for a set of ortho-normal wavefunctions is obtained by

$$N = 1 + \sum S_{ij}^2. \quad (9)$$

It can be shown that the terms in the wavefunction expansion are not mutually orthogonal. Hence, the normalization factor N is given in terms of

$$N = \sum_{a=0}^{NT-1} \sum_{b=0}^{NT-1} S_a S_b \quad (10)$$

with 0 referring to the reference configuration. Since the system contains k particle types, each containing n_k particles, the overall normalization constant becomes

$$N = \left(\prod_{i=1}^k n_i! \right) \sum_{a=0}^{NT-1} \sum_{b=0}^{NT-1} S_a S_b. \quad (11)$$

In principle, the optimised wavefunction also yields an optimised geometry for the system. The mean position of any given nucleus is given by

$$\langle r_i \rangle = \frac{\langle \Psi | \hat{r}_i | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (12)$$

Since ‘‘atom-centred’’ basis sets are used (in modified form or otherwise), it is necessary for the mean positions of the nuclei to be in the vicinity of the origins (centres) of the basis functions. Hence, the basis functions are translated to the new ‘positions’ of the nuclei as computed above. This is necessary as otherwise highly deformed wavefunctions may result, especially when input geometries are sufficiently different from the optimal geometry for the given set of basis functions. One of the convergence criteria would then be that the mean positions of the nuclei do not change from one iteration to the next. As noted above, the mean position of a given nucleus is given by

$$\langle r_i \rangle = \frac{\langle \Psi | \hat{r}_i | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (12)$$

Since the total wavefunction can be written as $\Psi = (1/\sqrt{N}) \sum_i [S_i \prod_{n=1}^k |\mathbf{D}_i^n|]$, after factoring in the normalization condition the above expression then becomes

$$\begin{aligned} \langle r_i \rangle &= \left\langle \sum_a S_a \prod_{n=1}^k |\mathbf{D}_a^n| \left| \hat{r}_i \right| \sum_a S_a \prod_{n=1}^k |\mathbf{D}_a^n| \right\rangle \\ &= \sum_a \sum_b S_a S_b \left\langle \prod_{n=1}^k |\mathbf{D}_a^n| \left| r_i \right| \prod_{n=1}^k |\mathbf{D}_b^n| \right\rangle. \end{aligned} \tag{13}$$

Integrating over all types of particles other than that of the nucleus of interest,

$$\langle r_i \rangle = \sum_a \sum_b S_a S_b \sum_{j,k} \langle \psi_j^a(r_i) r_i \psi_k^b(r_i) \rangle. \tag{14}$$

Expanding the single-particle wavefunctions as $\psi_j = \sum_x C_{xj} \chi_x$,

$$\langle r_i \rangle = \sum_a \sum_b S_a S_b \sum_j \sum_k \sum_x \sum_y C_{xj}^a C_{xy}^b \langle \chi_x r_i \chi_y \rangle. \tag{15}$$

In the case that real functions are used, corrections must be made for double counting. Hence,

$$\langle r_i \rangle = \frac{1}{2} \sum_a \sum_b S_a S_b \sum_j \sum_k \sum_x \sum_y C_{xj}^a C_{yk}^b \langle \chi_x r_i \chi_y \rangle. \tag{16}$$

Optimisation of the geometry allows one to converge only to stationary points respective to both electronic and nuclear coordinates simultaneously. Hence, the computation of the geometry by this method could yield either a minimum or a saddle point. Implementation of such a method would enable optimisation only to stationary points, such that the optimised result is a stationary point with respect to electronic and nuclear coordinates. Hence, one can gather that the only possible results would be optimisation to minima and saddle points. Identification of the same could be achieved by investigating the curvature at the final geometry.

In a true non-Born–Oppenheimer method, it is strictly not possible to think in terms of a definite molecular geometry. The concept of a molecular geometry (with known bond lengths and bond angles) suggests that the exact relative positions of the various atoms (nuclei) in the system are known. This would imply invocation of the Born–Oppenheimer approximation. However, the concept of a molecular geometry is something that is of great interest to chemists. All experimental determinations of the molecular geometries are necessarily time-averages of the various instantaneous orientations of the molecule over the time frame of the experiment. This involves computation of the mean positions of the nuclei in the system. The vectorial differences in position will lead to mean inter-nuclear separations and hence mean bond angles can also be calculated. As

the experimental determination yields a time-average position, this is analogous to the expectation value of the nuclear positions.

3. Notes on implementation

The method mentioned above is in the process of being implemented. A possible implementation scheme for this non-Born–Oppenheimer technique is outlined below.

In order to not bias the results of a calculation, and to avoid symmetry breaking effects (present in the energy terms beyond the zero order), the method must be implemented to run in C_1 symmetry. This is also necessary to avoid the difficulties involved when separating the various particle types, which are treated as being self-contained systems, each with its own symmetry. This is a relic of the manner in which quantum chemical codes have been implemented to date, as there was never a necessity to consider any more than the electrons in the system. It is also worth remembering that isotopic substitution leads to break of symmetry, and currently extant codes are not capable of accepting these differences. Hence, it is deemed prudent to ignore symmetry constraints and perform all calculations without symmetry.

As in any other implementation, the input should contain a guess geometry for the system of interest. In addition, it is necessary to specify the isotope for each atom in the system. The first step in the analysis involves the placing of the various particles in ‘boxes’, one for each particle type. The first box contains electrons; the other boxes are labelled as per the order of appearance in the input stream. The basis to be used is read in from the input file. The basis functions for the nuclei are generated internally based on the information provided by scaling the electronic basis functions at each centre. Since it is known that the effect of delocalisation of the nuclei is small, it is necessary to employ reasonably large basis sets on the nuclei to capture the effect accurately. The extent of scaling remains an open question. Clearly, the basis space for the nuclei—describing the extent of delocalisation—should necessarily be reduced in geometric extent relative to that of the electrons. This can be rationalized based on the knowledge that the de Broglie wavelength of a particle is inversely related to its mass. In modern computational chemical techniques, the delocalisation of the electron is approximated by means of a set of basis functions (typically Gaussian in behaviour but not necessarily so). The basis functions provide a means to approximate the extent of delocalisation of the electrons in a molecule. As most basis functions are of the form $\chi = Y_{l,m} e^{-\alpha r^2}$, the radial delocalisation is completely concentrated in the exponential term. Hence, it is reasonable to scale the exponential term to achieve the requisite behaviour for the nuclei. This cannot be attained by scaling the function by a scalar multiplicative factor, as the normalisation procedure would nullify its effects. It is therefore necessary to modify the radial

dependence by modifying the exponential part of the term. This is achieved by scaling the exponent by a factor of $(m/m_e)^{1/x}$, with the value of x left to be determined.

The value of x , though not known directly can be inferred from other sources. It may be recalled that based on the equipartition of kinetic energy, the total wavefunction was expanded in terms of $(m/m_e)^{1/4}$ [1, 2]. This yields a suggested value of $x = 4$. Bochevarov et al. [11] implemented the ENMO method in which a value of unity is employed for x . This may be due to expedience as no satisfactory explanation is proffered as to why this should be the case. Interestingly, Tachikawa and others [30] obtained a value of $x = 1.2$ for their basis set, when recalculated from the published exponents. In another work, Tachikawa and Osamura obtain values of x between 2.1 and 3.5 [31]. A strict comparison is complicated by the fact that the basis functions were optimised in the molecule and not for the free atom. Hence, the reported basis functions vary by the isotopomer, and not the isotope. Though the Tachikawa approach is valuable, it does not provide a general method to determine the scaling factors. There is also no information as to what the physically expected scaling factor must be, so a completely general means of generating scaling factors is required in order to be of widespread applicability. However, the similarity to the values predicted by Born and Oppenheimer lends credence to the view that the optimised value is dominated by the physically predicted equipartition principle.

The equipartition principle states that the energy contribution of each of the degrees of freedom in a system should be of the same order of magnitude [32]. Depending on the form of the specific potential, the various contributions differ by a simple multiplicative factor [32]. Hence, as a first approximation to the expected scaling factor, one can determine the scaling factor that would yield a nuclear kinetic energy similar in magnitude to the electronic kinetic energy. For simplicity's sake, one can consider a single electronic basis function χ and the scaled nuclear analogue χ' . If one were to consider a Gaussian shape for the basis function $\chi = e^{-\alpha r^2}$, then the nuclear function is $\chi' = e^{-\alpha' r^2}$ where $\alpha' = (q^{1/x})\alpha$. The ratio $q = (m/m_e)$ represents the mass of the nucleus in atomic units. One need not consider the angular contribution, as the angular contribution cancels out. For a Gaussian function, it can be shown that x is in the neighbourhood of $1/2$. Since a highly simplified case is presented here, it is likely that the actual value obtained may be significantly different from that predicted here. It is interesting that an analogous treatment for Slater functions yields an exact value of unity for x .

Once the basis functions are scaled and placed in boxes, the remainder of the problem is one for which a solution is already known: the unrestricted Hartree-Fock method. Prior to solving the UHF wavefunction by means of the Pople-Nesbet equations [33], it is necessary to generate a list of the various basis functions and their 'origins' (namely, which box they come from). This ensures

that the basis functions belonging to a certain box are only optimised within that box. Moreover, the ‘inter-box’ interactions need to be quantified and hence it is more convenient to generate a comprehensive list of all possible interactions and choose the relevant integrals as and when required. In this manner, one can retain the integrals necessary for the higher-order energy terms without resorting to regeneration of the same.

The \mathbf{H} matrix for each box is constructed from the \mathbf{T} matrix for each box. The other contribution to the \mathbf{H} matrix comes from the inter-box Coulombic interactions. For the sake of convenience, these will be referred to as \mathbf{J}_{ij} where the subscripts refer to the boxes connected by these terms. From the guess functions, the \mathbf{P} matrices for each box can be generated. The density distribution matrix \mathbf{D} is generated according to the property $D(i, j) = S(i, j)P(i, j)$, where the \mathbf{S} matrix is the (previously defined) overlap matrix relevant to the box. This matrix denotes the distribution of particle density as a function of the basis, whereas the \mathbf{P} matrix signifies the occupation distribution along the same axis. The \mathbf{H} matrix for a given box i can then be given by

$$\mathbf{H}_i = \mathbf{T}_i + \sum_{j \neq i} \mathbf{D}_j \mathbf{J}_{ij}. \quad (17)$$

This includes all the interactions except the Coulomb and exchange interactions present within each box. The intra-box Coulomb interactions are introduced *via* the \mathbf{G} matrix. Solving the Pople-Nesbet equations then optimises the density matrix \mathbf{P} (by optimising the coefficient matrix). Since the \mathbf{H} matrix remains unchanged during the optimisation of the coefficient matrix for a box, the \mathbf{H} matrix needs to be updated based on the new \mathbf{P} matrices generated. One cycle wherein the SCF convergence for each particle type is performed is defined as an epoch. The \mathbf{H} matrices are only updated at the end of each epoch. Hence, it can be considered that the convergence of the \mathbf{H} matrices be a condition of convergence of the system. It is to be remembered that the \mathbf{T} matrix remains constant for any given geometric configuration. Hence, convergence of the \mathbf{H} matrix implies convergence of the \mathbf{P} matrices.

It may be recalled that the computation of energy in the Pople-Nesbet (UHF) method is related to the density distributions (\mathbf{P}^α and \mathbf{P}^β matrices) through the \mathbf{H} and \mathbf{F} matrices, where \mathbf{F} is the sum of the \mathbf{H} and \mathbf{G} matrices. The UHF energy is given by

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} \left[\mathbf{P}_{\nu\mu}^T \mathbf{H}_{\mu\nu} + \mathbf{P}_{\nu\mu}^\alpha \mathbf{F}_{\mu\nu}^\alpha + \mathbf{P}_{\nu\mu}^\beta \mathbf{F}_{\mu\nu}^\beta \right]. \quad (18)$$

In an analogous fashion, the energy of each box can be computed by

$$E^i = \frac{n^i!}{2N_0} \sum_{\mu} \sum_{\nu} \left[\mathbf{P}_{\nu\mu}^{T,i} \left(\frac{\mathbf{H}_{\mu\nu}^i + \mathbf{T}_{\mu\nu}^i}{2} \right) + \sum_s^{\text{spins}} \mathbf{P}_{\nu\mu}^{s,i} \mathbf{F}_{\mu\nu}^{s,i} \right]. \quad (19)$$

The term $N_0 = \prod_{i=0}^k (n^i!)$ is the overall particle normalization term that enables the energies to be additive, and n^i is the number of particles in a given box i . This is necessary as each box is internally normalized by $n^i!$. It may be recalled that $\mathbf{H} = \mathbf{T} + \mathbf{V}$. In this case, the \mathbf{V} terms relate to the Coulomb interactions involving particles in a given box and all other boxes. The full magnitude of the force is seen by the particle through the \mathbf{H} matrix. However, to include the full magnitude in the energy computation would lead to a double counting (and hence over-estimation) of the Coulomb energy between dissimilar particles. In order to correct for this, the ‘single particle’ energy is given by $\mathbf{P} (\mathbf{T} + \mathbf{V}/2)$, and it can be trivially shown that this leads to the result shown above. The zero-order energy of the system (term 00), is then

$$E_{00} = \sum_{i=0}^k E^i. \tag{20}$$

Once the energies are computed for the higher-order correction terms, one can then generate the total energy of the system using

$$E = \frac{\sum_{a,b} E_{ab}}{\sum_{a,b} S_a S_b}. \tag{21}$$

The computation of the higher order correction terms is carried out in an analogous fashion. A combined coefficient matrix is generated from the individual \mathbf{C} matrices such that the columns of the combined (\mathbf{C}^\bullet) matrix are taken from the \mathbf{C} matrices. The \mathbf{C}^\bullet matrix has dimension of the $K \times \sum_B N_B$. Hence, the \mathbf{C}^\bullet matrix for the reference configuration is a block diagonal matrix. Particle interchange is achieved by interchanging the columns corresponding to the particle indices of the particles being interchanged. The \mathbf{P} and \mathbf{D} matrices are then obtained as products over rectangular matrices. The energy computation for the higher order correction terms can then be performed as outlined above.

4. Computational expense and scaling

There are two components to the time requirement. The initial component is the time required for SCF convergence. As the SCF convergence is carried out in several ‘boxes’ independently and serially, the time requirement increases as the number of boxes and the fourth power of the number of basis functions in each box. This requirement is identical to the time requirement for a Hartree-Fock computation on each box separately. The time required for SCF convergence (barring difficult convergence cases) increases as $T^{SCF} \sim \sum_{\text{boxes}} N_B^4$ where N_B is the number of basis functions in box B .

By far the largest contribution to the time required for a computation is the post-processing step. This is greatly affected by the number of ‘configurations’ to be included in the computation. The number of configurations increases

with the number of particles and the number of boxes in the system. It is, in a sense, a measure of the amount of flexibility in a system. As a rough approximation, the number of configurations is given by kK , and the number of energy terms is given by the square of the number of configurations. Hence, isotopic substitution becomes a factor that affects the computational requirements, as it increases the number of boxes in the system. It has been found that when real basis functions are used, the number of energy terms one need compute is nearly halved, as the off-diagonal terms are identical. Within each energy term, the time expense varies as $(\sum_{\text{boxes}} N_B)^4$, leading to an overall post-processing time that varies as $[kK]^2 (\sum_{\text{boxes}} N_B)^4$. For all systems, this is the limiting step in terms of the computational resources. It is for this reason that it is recommended that the post-processing only be performed on the optimised densities and not during intermediate steps. It is evident that the total number of computations to be performed is severely dependent on the basis set employed, as the computational time increases rapidly with the total number of basis functions.

5. Discussion

The current method by its construction was required to fit certain conditions. Among these is the requirement that the molecular wavefunction should not be separable into electronic and nuclear contributions. This means that it should not be possible for the molecular wavefunction to be expressed as $\Psi = \psi_e \psi_n$ or simply as $\Psi = \sum_i \sum_j \psi_e^i \psi_n^j$, since the latter can be rearranged to $\Psi = (\sum_i \psi_e^i) (\sum_j \psi_n^j)$. Obviously, this latter representation is only a restatement of the initial approximation. It is therefore necessary that the molecular wavefunction be expressed as a sum of products, where the terms of the series are non-factorable into nuclear and electronic terms. In the current method, the total molecular wavefunction is given by

$$\Psi = \frac{1}{\sqrt{N}} \sum_i \left[S_i \prod_{n=1}^{\text{fermions}} |D_i^n| \prod_{n=1}^{\text{bosons}} |D_i^n|_+ \right]. \quad (4)$$

In the above equation, the summation is over various ‘configurations’ where the configuration space extends over the molecular orbital space computed under the separability approximation. The available space for a particle includes the ‘orbital’ space of every type of particle in the system with the probability of particle interchange being governed by the overlap integral of the two occupied functions. This scaling of the overlap makes it impossible to factorise the molecular wavefunction into separable components, thus satisfying the primary requirement of a truly non-Born–Oppenheimer method. However, due to the formation of an electron-nucleus coupled wavefunction, one can strictly no longer

consider the system as a collection of occupied MOs. The system is now specified only in terms of a state, described by the wavefunction. Of course, this was always expected for a true *ab initio* method, though recent history has run contrary to such views. It has been customary to think of a molecule in terms of an electronic state (or even assemblage of MOs), assuming that the nuclei offer nothing more than the Coulombic potential background on which the electrons interact.

As is obvious from the implementation described previously in this section, the nuclei have been ‘placed’ in orbitals and hence the nuclei are necessarily delocalised. Since the extent of delocalisation is a factor of the mass of the particle, it can be seen that the deviation from Born–Oppenheimer behaviour is small for the heavier nuclei and larger for the lighter nuclei. This is consistent with expectations, as the basis of the BO approximation is the separability of nuclear and electronic motion due to the large mass ratio. This would tend to be a more valid assumption as the nucleus increases in mass.

Another important feature of this method is the introduction of interchange between particles of different types. This leads to an increased region of delocalisation for the nuclei. At the same time, this increases the concentration of the electronic density in the region of the mean positions of the nuclei. It is also noteworthy that no effort is made to correct for the cusp at the nuclear positions. This is because the cusp is an artefact of the Born–Oppenheimer approximation. The cusp originates from the fact that an electron cannot occupy the same position as a nucleus, leading to a singularity. Since the nuclei are no longer required to be clamped in position, there is no necessity to have a singularity (cusp) at the nuclear positions. Since the nuclei are treated as quantum particles, they occupy a region of space that is given by the wavefunction. The electronic wavefunction must satisfy the Hamiltonian operator used in conjunction with the nuclear charge distribution (as described by the nuclear MO). As the nuclei are represented as continuum charge distributions, there cannot exist a cusp in the electronic wavefunction at the mean nuclear position. This is analogous to the result obtained when employing the finite-nucleus model [34]. However, the tendency for an increased electron density in the vicinity of the nuclear positions is undiminished, and satisfied by the interchange principle built into the model. Hence, the interchange principle serves two purposes. It helps to improve the particle density distributions while at the same time making the wavefunction non-separable (non-factorisable) into separate electronic and nuclear contributions.

6. Conclusions

A non-Born–Oppenheimer SCF method has been outlined and some salient features of a possible implementation have been outlined. The computational

expense of this method prevents it from being of general applicability. An implementation should allow the effect of isotopic substitution to be calculated using this method. A further discussion of the method development is also available [35].

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References

- [1] M. Born and R. Oppenheimer, *Ann. Physik* 84 (1927), 457.
- [2] M. Born and R. Oppenheimer, in: *Quantum Chemistry: Classic Scientific Papers*, ed. H. Hettema (World Scientific, Singapore, 2000), pp. 1–24.
- [3] I.L. Thomas, *Phys. Rev.* 185 (1969), 90.
- [4] I.L. Thomas, *Phys. Rev. A* 2 (1970), 728.
- [5] I.L. Thomas and H.W. Joy, *Phys. Rev. A* 2 (1970), 1200.
- [6] I.L. Thomas, *Phys. Rev. A* 2 (1970), 1675.
- [7] I.L. Thomas, *Phys. Rev. A* 3 (1971), 565.
- [8] I.L. Thomas, *Phys. Rev. A* 3 (1971), 1022.
- [9] I.L. Thomas, *Phys. Rev. A* 4 (1971), 457.
- [10] I.L. Thomas, *Phys. Rev. A* 5 (1972), 1104.
- [11] A.D. Bochevarov, E.F. Valeev, C.D. Sherrill, *Mol. Phys.* 102 (2004), 111.
- [12] W. Koch and M.C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, 2001).
- [13] J.A. Coxon and R. Colin, *J. Mol. Spect.* 181 (1997), 215.
- [14] Y. Shigeta, H. Nagao, K. Nishikawa, K. Yamaguchi, *Int. J. Quant. Chem.* 75 (1999), 875.
- [15] N.C. Handy, Y. Yamaguchi, H. F. Schaefer, III, *J. Chem. Phys.* 84 (1986), 4481.
- [16] H. Sellers and P. Pulay, *Chem. Phys. Lett.* 103 (1984), 463.
- [17] W. Kolos and L. Wolniewicz, *Phys. Lett.* 2 (1962), 222.
- [18] W. Kolos and L. Wolniewicz, *Rev. Mod. Phys.* 35 (1963), 473.
- [19] B.A. Pettitt, *Thesis: Two Topics in Theoretical Chemistry: A: Nuclear Spin Hamiltonian Operators and Simulation of Magnetic Resonance Spectra; B: Proton Self-Consistent Fields in Hydride Molecules* (Dalhousie University, Halifax, NS, 1985).
- [20] B.A. Pettitt, *Chem. Phys. Lett.* 130 (1986), 399.
- [21] M. Cafiero and L. Adamowicz, *Chem. Phys. Lett.* 387 (2004), 136.
- [22] M. Cafiero and L. Adamowicz, *J. Chem. Phys.* 116 (2002), 5557.
- [23] M. Cafiero, S. Bubin, L. Adamowicz, *PCCP*, 5 (2003), 1491.
- [24] M. Cafiero and L. Adamowicz, *Phys. Rev. Lett.* 89 (2002), 073001/1-01/4.
- [25] M. Cafiero and L. Adamowicz, *Phys. Rev. Lett.* 88 (2002), 033002/1-02/4.
- [26] M. Cafiero, L. Adamowicz, M. Duran, J.M. Luis, *Theochemistry* 633 (2003), 113.
- [27] P.-O. Löwdin, *J. Mol. Struct. (Theochem)*. 230 (1991), 13.
- [28] W. Pauli, *Phys. Rev.* 58 (1940), 716.
- [29] R. Shankar, *Principles of Quantum Mechanics* (Kluwer Academic, New York, New York, 1994).

- [30] M. Tachikawa, K. Mori, H. Nakai, K. Iguchi, *Chem. Phys. Lett.* 290 (1998), 437.
- [31] M. Tachikawa and Y. Osamura, *Theor. Chem. Acc.* 104 (2000), 29.
- [32] J.A.S. Lima and A.R. Plastino, *Braz. J. Phys.* 30 (2000), 176.
- [33] J.A. Pople and R. K. Nesbet, *J. Chem. Phys.* 22 (1954), 571.
- [34] F. Jensen, *Introduction to Computational Chemistry* (John Wiley & Sons, 2001).
- [35] B. Viswanathan, *Thesis: The Development of a Non-Born-Oppenheimer Self-Consistent Field Method and Computational Cluster Studies on the Solvation of Cations and Anions* (Dalhousie University, Halifax, NS, 2005).