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Abstract

We introduce the electron-nuclei general mean field configuration interaction (EN-GMFCI) approach. It consists in building an effective Hamiltonian for the electrons taking into account a general mean field due to the nuclear motion and, conversely, in building an effective Hamiltonian for the nuclear motion taking into account a general mean field due to the electrons. The eigenvalue problem of these Hamiltonians are solved in a basis set giving partial eigensolutions for the active degrees of freedom (dof), that is to say, either for the electrons or for the nuclear motion. The process can be iterated. If first-order effective Hamiltonians, averaged over the ground state (GS) of the non-active or "spectator" dof, are chosen at every step of the process, the total energy corresponding to the product of the electronic GS wave functions by the nuclear motion GS wave function, can only decrease. The EN-GMFCI is a new paradigm for quantum chemistry that bypasses the traditional Born-Oppenheimer (BO) reduction of the molecular Schrödinger equation to an electronic problem and a nuclear poblem. In the EN-GMFCI method, electron and nuclei are treated on the same footing. In contrast with the BO or adiabatic decoupling schemes, the electronic potential for the nuclei is known exactly and analytically from a single electronic calculation. So there is no need to perform electronic calculations for a large grid of nuclear configurations and to fit a PES. The method is illustrated on diatomic molecules.

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1 Introduction

The Born-Oppenheimer (BO) potential energy surface (PES) is one of the main paradigm of quantum chemistry since its origin [1]. It has proved very successful in solving many molecular spectroscopy and molecular dynamics problems. The BO approximation has been found more accurate than one could expect due to some error compensation between the adiabatic correction and mass polarisation contributions [2]. However, they are a number of conceptual and practical problems with the BO PES approach. To quote a few: Its mathematical justification is not yet completely satisfactory [3]. The generalisation of the PES concept to a non-adiabatic context hits the difficulty that a PES should not be regarded as an observable but rather as a quotient of observables [4]. The number of points needed to described accurately a full-dimensional PES grows dramatically as the number of nuclei increases, and the number of electronic Schrödinger equations to be solved grows accordingly. The represention of a full-dimensional PES, only known at a discrete set of points, by a continuous function, is also an issue for the actual use of a PES in many applications. Many technical choices must be adressed such as how to select the nuclear configurations where the PES is evaluated, should the derivatives at these points be calculated or not, if using finite differences what should be the stepsize, should one use an interpolation scheme or a global analytical function, how to insure the correct asymptotical behaviour, how to estimate the goodness of the fit...

The purpose of the present article is to show that the construction of a BO PES can be bypassed and that one can still obtain very accurate vibronic energy levels.

Existing methods to deal with non-BO systems usually starts with the BO approach and then couples BO excited electronic states. These methods are limited to small systems and a limited number of BO excited electronic states, since they require the computation of one PES per electronic state. Very few groups worldwide have developed methods dealing on an equal footing with electron and nuclei degrees of freedom. There is essentially one and the same method developed under different names by different groups:
- The FVMO (full variational treatment of molecular orbital) method of Tachikawa et

al. [5], later called with a different name, DEMO (dynamic extended molecular orbital) method [6], later called NOMO (nuclear orbital molecular orbital by Nakai et al. [7];
- The CMFT-GCM (coupled mean-field theory- generator coordinate method) of Shigeta et al. [8] who later turned towards non-BO DFT;
- The NEO (nuclear-electronic orbital) method [9].
More recently, a method based on explicitly correlated geminal Gaussian basis function, inspired by the pioneering work of Cafiero and Adamowicz [10] has been proposed by Matyus and Reiher [11]. So far, the success of all these methods has been limited, mainly because the coordinates and/or the basis sets used for the nuclear degrees of freedom were not amenable to describe sufficiently excited vibrational states. Furthermore, these approaches usually start from a global single determinantal wave function for all degrees of freedom. That is to say, they have to recover electronic correlation, vibrational correlation and electron-vibration correlation all at once. These drawbacks will be avoided in the GMFCI approach.

The MFCI method [12–15] is a general approach that has proved very effective to solve the vibrational Schrödinger equation. It consists in successive couplings of groups of degrees of freedom called "active" in the mean field of the other degrees of freedom called "spectators". After each step, the eigenstates corresponding to energy eigenvalues that are too high to be useful to the description of the physical states of interest, are discarded. This way, the size of the configuration space can remain tractable regardless of the number of atoms in the molecule. Recently, the use of more general mean field expressions arising from perturbation theory has been proposed [16], giving increased flexibility: the so-called "GMFCI" method.

Here, we propose to generalize the GMFCI ideas to a set of both electrons and nuclei. Rotational dof will be omitted from now on, to simplify the discussion, although they could be included in a similar fashion as vibrational dof. This issue will be discussed in conclusion. First, we will obtain a basis set of vibrational wave functions by diagonalizing a mean field vibrational Hamiltonian. The latter will only require a realistic zero order fundamental electronic wave function. It will not require a BO PES as in the traditional

approach but a mean field PES. Provided Gaussian type orbitals (GTO) are used to describe the electronic wave function, this mean field PES admits an analytical expression in terms of confluent hypergeometric functions. However, such an expression is not even needed in practice, only its integrals over vibrational basis functions are required. When traditional harmonic oscillator (HO) basis functions are used to describe the vibratonal wave functions, double Rys quadrature [17–20] is a very practical way to calculate the required integrals.

Similarly, we will need to obtain a basis set of electronic wave functions by diagonalizing an electronic Hamiltonian averaged over the vibrational ground state. Here again, special functions may appear in this mean field Hamiltonian. Numerical quadrature integration will be used to compute efficiently the integrals as for the vibrational degrees of freedom.

Finally, the new integrals appearing in the GMFCI step contracting vibrational and electronic degrees of freedom together, will be of the same nature, despite the fact that they will involve excited state basis functions in addition to fundamental state basis functions. The same quadrature routines will be used again.

The article is organized has follows: First the general frame of the GMFCI method for electrons and nuclei is presented. Then, we provide some technical but essential details on the calculation of integrals required in the Hamiltonian matrix element evaluations for the case of a diatomic molecule. Finally, we conclude on the prospects of the method.

2 The GMFCI method for electrons and nuclei

Although the degrees of freedom (dof) are entangled in a quantum world, from an operational point of view, i.e. for all practical purposes, they appear dynamically autonomous. It thus makes sense physically to consider them independently in the mean field of the others in first approximation, and then if this approximation proves too rough, to couple some dof to refine the description.

2.1 General setting

Let us consider a molecule made of p electrons and N nuclei. We denote collectively by $\vec{R}^e := (\vec{r}_1{}^e, \vec{r}_2{}^e, \ldots, \vec{r}_p{}^e)$, the electronic position variables with respect to the center of nuclear mass, by $\vec{R}^n := (\vec{r}_1{}^n, \vec{r}_2{}^n, \ldots, \vec{r}_N{}^n)$, the nuclear position variables in the same frame, and by $\vec{Q} := (Q_1, Q_2, \ldots, Q_q)$ mass-weighted Cartesian normal coordinates, with $q = 3N - 5$ or $q = 3N - 6$ depending upon the molecule being linear or not. The $\vec{Q}$ are related to displacements, $\Delta\vec{R}^n = \vec{R}^n - \vec{R}^0$, with respect to a reference nuclear geometry, $\vec{R}^0 = (\vec{r}_1{}^0, \vec{r}_2{}^0, \ldots, \vec{r}_N{}^0)$, in an Eckart frame [21] by two linear operators,

$$\vec{Q} = \hat{L}\hat{G}\Delta\vec{R}^n. \tag{1}$$

$\hat{G}$ is represented by a $(3N \times 3N)$ diagonal matrix containing the square roots of the nuclear masses, and $\hat{L}$ by a $(q \times 3N)$ matrix whose lines are orthonormals. So, at nuclear configurations where the translation and rotation mass-weighted Cartesian coordinates are zero (or considered as zero) the above formula can be inverted as

$$\vec{R}^n = \hat{G}^{-1}\hat{L}^T\vec{Q} + \vec{R}^0, \tag{2}$$

where $\hat{L}^T$ is the transposed of $\hat{L}$. In particular,

$$\vec{r}_a{}^n = \hat{G}_a^{-1}\hat{L}^T\vec{Q} + \vec{r}_a{}^0, \tag{3}$$

$\hat{G}_a^{-1}$ being the $(3 \times 3N)$ submatrix of $\hat{G}^{-1}$ corresponding to nucleus a.

We decompose the molecular Hamiltonian into three parts:
a purely electronic one,

$$\hat{H}(\vec{R}^e) = -\frac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r}_i^e} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i{}^e - \vec{r}_j{}^e\|}, \tag{4}$$

a purely vibrational one,

$$\hat{H}(\vec{Q}) = -\frac{1}{2}\sum_{i=1}^{q}\Delta_{Q_i} + \sum_{1\le a<b\le N}\frac{Z_aZ_b}{\|\vec{r}_a{}^0 - \vec{r}_b{}^0 + \hat{G}_a^{-1}\hat{L}^T\vec{Q} - \hat{G}_b^{-1}\hat{L}^T\vec{Q}\|}, \tag{5}$$

and a coupling term,

$$\hat{H}(\vec{R}^e,\vec{Q}) = -\sum_{i=1}^{p}\sum_{a=1}^{N}\frac{Z_a}{\|\vec{r}_i^{\,e} - \vec{r}_a^{\,0} - \hat{G}_a^{-1}\hat{L}^T\vec{Q}\|}. \tag{6}$$

Eq. (3) allows one to recognise Coulomb potential terms on the right-hand side of Eqs.(5) and (6).

It is out of the scope of the present article to review the involved procedure that one has to follow in order to derive such an Hamiltonian from the usual Coulomb Hamiltonian for nuclei and electrons [3,22]. We will not attempt to justify the omission of many terms that are not included in Eqs. (4) to (6) for the sake of simplifying the presentation. Eliminating translations [2], for example, introduces mass-polarization terms and reduced-mass corrections that are neglected here. The separation of rotational motion for electronic dofs also imposes the neglect of terms involving the electronic angular momenta [23,24]. The full rovibrational Eckart-Watson Hamiltonian [25,26,21] could have been introduced, however, here, as in many studies limited to vibrational motion, rotational dof and Coriolis couplings are omitted.

2.2 General Mean field Hamiltonian for the electrons

Let us call $\phi_{\vec{0}}^{(0)}(\vec{Q})$ a zero-order approximation of the vibrational GS. We build a first order mean field Hamiltonian for the electrons according to

$$\begin{aligned}\hat{H}^{eff}(\vec{R}^e) &= \hat{H}(\vec{R}^e) + \langle\phi_{\vec{0}}^{(0)}(\vec{Q})|\hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e,\vec{Q})|\phi_{\vec{0}}^{(0)}(\vec{Q})\rangle_{\vec{Q}}\\ = -\frac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r}_i^{\,e}} &+ \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i^{\,e} - \vec{r}_j^{\,e}\|} - \sum_{i=1}^{p}\sum_{a=1}^{N}\langle\phi_{\vec{0}}^{(0)}(\vec{Q})|\frac{Z_a}{\|\vec{r}_i^{\,e} - \vec{r}_a^{\,0} - \hat{G}_a^{-1}\hat{L}^T\vec{Q}\|}|\phi_{\vec{0}}^{(0)}(\vec{Q})\rangle_{\vec{Q}}\\ +\langle\phi_{\vec{0}}^{(0)}(\vec{Q})| -\frac{1}{2}\sum_{i=1}^{q}\Delta_{Q_i} &+ \sum_{1\le a<b\le N}\frac{Z_aZ_b}{\|\vec{r}_a^{\,0} - \vec{r}_b^{\,0} + \hat{G}_a^{-1}\hat{L}^T\vec{Q} - \hat{G}_b^{-1}\hat{L}^T\vec{Q}\|}|\phi_{\vec{0}}^{(0)}(\vec{Q})\rangle_{\vec{Q}},\end{aligned} \tag{7}$$

where $\langle|\rangle_{\vec{Q}}$ means that integration is carried out only for vibrational coordinates. So, the last bracket on the right-hand side is just a constant.

The clamped nuclei approximation can be seen as a particular case, where $\phi_{\vec{0}}^{(0)}(\vec{Q}) = \bigotimes_{i=1}^{q} \delta_0(Q_i)$, the tensor product of Dirac distributions centered at zero, provided that the nuclear kinetic energy, which is ill-defined in this case, is left out,

$$\hat{H}^{cn}(\vec{R}^e) = -\frac{1}{2}\sum_{i=1}^{p} \Delta_{\vec{r}_i^{\,e}} + \sum_{1\leq i<j\leq p} \frac{1}{\|\vec{r}_i^{\,e} - \vec{r}_j^{\,e}\|} - \sum_{i=1}^{p}\sum_{a=1}^{N} \frac{Z_a}{\|\vec{r}_i^{\,e} - \vec{r}_a^{\,0}\|} + \sum_{1\leq a<b\leq N} \frac{Z_a Z_b}{\|\vec{r}_a^{\,0} - \vec{r}_b^{\,0}\|}. \tag{8}$$

Alternatively, one can choose $\phi_{\vec{0}}^{(0)}(\vec{Q}) = \bigotimes_{i=1}^{q} \phi_0^i(Q_i)$, a product of GS eigenfunctions of some one-dimensional model Hamiltonians, as a guess to initiate the EN-GMFCI process. Then, approximate excited states represented by, $\phi_{\vec{K}}^{(0)}(\vec{Q}) = \bigotimes_{i=1}^{q} \phi_{k_i}^i(Q_i)$, $\vec{K} = (k_1, \ldots, k_q)$, that is to say, products of k_i^{th}-excited functions, can be used to build a more general MF Hamiltonian, for instance, a second order GMF Hamiltonian [16],

$$\begin{aligned} \hat{H}^{eff}(\vec{R}^e) &= \hat{H}(\vec{R}^e) + \langle\phi_{\vec{0}}^{(0)}(\vec{Q})|\hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e,\vec{Q})|\phi_{\vec{0}}^{(0)}(\vec{Q})\rangle_{\vec{Q}} \\ &+ \sum_{\vec{K}\neq(0,\cdots,0)} \frac{\langle\phi_{\vec{0}}^{(0)}(\vec{Q})|\hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e,\vec{Q})|\phi_{\vec{K}}^{(0)}(\vec{Q})\rangle_{\vec{Q}}\langle\phi_{\vec{K}}^{(0)}(\vec{Q})|\hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e,\vec{Q})|\phi_{\vec{0}}^{(0)}(\vec{Q})\rangle_{\vec{Q}}}{E_{\vec{0}}^{(0)} - E_{\vec{K}}^{(0)}}, \end{aligned} \tag{9}$$

where the energy difference, $E_{\vec{0}}^{(0)} - E_{\vec{K}}^{(0)} = -\sum_{i=1}^{q}(E_{k_i}^i - E_0^i)$, is the opposite of the sum of 1D model Hamiltonian excitation energies. Such an expression is reminiscent of that of Bunker and Moss [27] obtained by contact transformation, which account for non adiabatic corrections to the electronic energy.

2.3 General Mean field Hamiltonian for the vibrational dof

Assuming that a GMF Hamiltonian, Eq.(8) for example, has been chosen to start the EN-GMFCI process, one can solve the Schrödinger stationary equation by any electronic calculation method, such as Hartree-Fock [28–31], configuration interaction [32], geminal-MFCI [13,33,34], or other available ansätze. Let us call, $\phi_{\vec{0}}^{(1)}(\vec{R}^e)$, an approximate solution for the electronic ground state. It can be used in turn to obtain an effective, first order,

vibrational Hamiltonian,

$$\begin{aligned}\hat{H}^{eff}(\vec{Q}) &= \hat{H}(\vec{Q}) + \langle\phi_{\vec{0}}^{(1)}(\vec{R}^e)|\hat{H}(\vec{R}^e) + \hat{H}(\vec{R}^e,\vec{Q})|\phi_{\vec{0}}^{(1)}(\vec{R}^e)\rangle_{\vec{R}^e} \\ &= -\frac{1}{2}\sum_{i=1}^{q}\Delta_{Q_i} + \sum_{1\le a<b\le N}\frac{Z_a Z_b}{\|\vec{r}_a^{\,0} - \vec{r}_b^{\,0} + \hat{G}_a^{-1}\hat{L}^T\vec{Q} - \hat{G}_b^{-1}\hat{L}^T\vec{Q}\|} \\ +\langle\phi_{\vec{0}}^{(1)}(\vec{R}^e)| &- \frac{1}{2}\sum_{i=1}^{p}\Delta_{r_i^e} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i^{\,e} - \vec{r}_j^{\,e}\|} - \sum_{i=1}^{p}\sum_{a=1}^{N}\frac{Z_a}{\|\vec{r}_i^{\,e} - \vec{r}_a^{\,0} - \hat{G}_a^{-1}\hat{L}^T\vec{Q}\|}|\phi_{\vec{0}}^{(1)}(\vec{R}^e)\rangle_{\vec{R}^e},\end{aligned} \tag{10}$$

where $\langle|\rangle_{\vec{R}^e}$ means that integration is carried out only for electronic coordinates. If one manages to obtain excited electronic wave functions, then, a higher order, effective Hamiltonian, similar to Eq.(9), can also be considered. However, sticking to first order MF Hamiltonians, averaged over spectator ground states, the GS energy of the active set always corresponds to the total energy of the product of GS wave functions. So, if one alternates the resolution of electronic and vibrational MF Hamiltonians by using a variational method, which can only lower the energy, one can expect to converge towards a self-consistent solution, as in the vibrational mean field configuration interaction (VMFCI) method [14,15].

In such an iterative process, at even iteration number ($m = 2l$) one solves an electronic problem (eigenvalue equation for the Hamiltonian given by Eq. (7) with $\phi_{\vec{0}}^{(0)}(\vec{Q})$ substituted by $\phi_{\vec{0}}^{(2l)}(\vec{Q})$). One obtains an electronic GS wave function, $\phi_{\vec{0}}^{(2l+1)}(\vec{R}^e)$. In turn, this wave function is used to build the vibrational MF Hamiltonian (according to Eq. (10) with $\phi_{\vec{0}}^{(1)}(\vec{R}^e)$ replaced by $\phi_{\vec{0}}^{(2l+1)}(\vec{R}^e)$) for the next iteration.

In contrast with NOMO and NEO approaches, electronic correlation can be taken into account from the start, if one uses a correlated method to obtain $\phi_{\vec{0}}^{(1)}(\vec{R}^e)$. The same is true for vibrational motion correlation. However, electron-nuclei coupling is only included in a MF fashion. If, eventually, it appears necessary to have a more accurate description of electron-nuclei correlation, then one can contract electronic and vibrational dof.

3 Integrals for diatomics

Let us first consider the case of a diatomic molecule and standard MFCI, that is to say order 1 GMFCI, equations. $\vec{Q}$ reduces to one scalar component that we denote simply by Q, dropping the component index. Assuming that the molecule lies along the z-axis of a body-fixed frame, Q will be the Cartesian displacement along z weighted by the reduced mass of the nuclei, $\mu_{ab} = \frac{m_a m_b}{m_a+m_b}$,

$$Q = \sqrt{\mu_{ab}}(r_{a_z} - r^0_{a_z} - r_{b_z} + r^0_{b_z}), \tag{11}$$

that is to say,

$$\hat{L} = (0, 0, +\frac{\sqrt{m_b}}{\sqrt{m_a+m_b}}, 0, 0, -\frac{\sqrt{m_a}}{\sqrt{m_a+m_b}}). \tag{12}$$

Its range is $]-\xi^0_{ab}, +\infty[$, where $\xi^0_{ab} = \|\sqrt{\mu_{ab}}(\vec{r}_a{}^0 - \vec{r}_b{}^0)\|$. It follows easily that,

$$\hat{G}_a^{-1}\hat{L}^T\vec{Q} = \begin{pmatrix} 0 \\ 0 \\ \frac{+\sqrt{\mu_{ab}}Q}{m_a} \end{pmatrix}, \qquad \hat{G}_b^{-1}\hat{L}^T\vec{Q} = \begin{pmatrix} 0 \\ 0 \\ \frac{-\sqrt{\mu_{ab}}Q}{m_b} \end{pmatrix}.$$

So, Eq. (10) becomes,

$$\hat{H}^{eff}(Q) = -\frac{1}{2}\sum_{i=1}^{q}\Delta_{Q_i} + \frac{\sqrt{\mu_{ab}}Z_aZ_b}{|\xi^0_{ab}+Q|} + \langle\phi_{\vec{0}}^{(1)}(\vec{R^e})| - \frac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r_i^e}} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i{}^e - \vec{r}_j{}^e\|}$$
$$-\sum_{i=1}^{p}\frac{Z_a}{\sqrt{(r^e_{i_x})^2 + (r^e_{i_y})^2 + (r^e_{i_z} - r^0_{a_z} - \frac{\sqrt{\mu_{ab}}Q}{m_a})^2}} + \frac{Z_b}{\sqrt{(r^e_{i_x})^2 + (r^e_{i_y})^2 + (r^e_{i_z} - r^0_{b_z} + \frac{\sqrt{\mu_{ab}}Q}{m_b})^2}}|\phi_{\vec{0}}^{(1)}(\vec{R^e})\rangle_{\vec{R^e}}, \tag{13}$$

and Eq. (7) becomes,

$$\hat{H}^{eff}(\vec{R^e}) = -\frac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r_i^e}} + \sum_{1\le i<j\le p}\frac{1}{\|\vec{r}_i{}^e - \vec{r}_j{}^e\|} + \langle\phi_0^{(0)}(Q)| - \frac{1}{2}\Delta_Q + \frac{\sqrt{\mu_{ab}}Z_aZ_b}{|\xi^0_{ab}+Q|}$$
$$-\sum_{i=1}^{p}\frac{Z_a}{\sqrt{(r^e_{i_x})^2 + (r^e_{i_y})^2 + (r^e_{i_z} - r^0_{a_z} - \frac{\sqrt{\mu_{ab}}Q}{m_a})^2}} + \frac{Z_b}{\sqrt{(r^e_{i_x})^2 + (r^e_{i_y})^2 + (r^e_{i_z} - r^0_{b_z} + \frac{\sqrt{\mu_{ab}}Q}{m_b})^2}}|\phi_0^{(0)}(Q)\rangle_Q. \tag{14}$$

Let us consider first the latter equation. In general, the vibrational GS wave function, $\phi_0(Q)$, will be expressed in terms of a model Hamiltonian eigenfunction basis set. In the

diatomic case, a harmonic model potential is not suitable, since the nuclear Coulomb integrals will diverge. So, we choose a Kratzer potential basis set, which is not only more accurate but also leads convergent nuclear Coulomb integrals.

$$\phi_0(Q) = \sum_{i=0}^{n_{max}} c_{0i}\phi_i^{kra}(Q), \tag{15}$$

where $\phi_i^{kra}(Q)$ is the ith eigenfunction of a Hamiltonian with Kratzer potential, $D\left(\frac{Q}{Q+\xi_{ab}^0}\right)^2$ [35,36]. However, to initiate the MFCI process, this expansion will be limited to the term $i = 0$ [36],

$$\phi_0^{(0)}(Q) = \frac{[2(\lambda-1)]^{\lambda+\frac{1}{2}}}{\sqrt{\xi_{ab}^0\Gamma[2\lambda+1]}}\left(1+\frac{Q}{\xi_{ab}^0}\right)^{\lambda} Exp\left[(1-\lambda)(1+\frac{Q}{\xi_{ab}^0})\right], \tag{16}$$

where $\Gamma[x]$ is the gamma function and λ is a constant,

$$\lambda = \frac{1}{2} + \sqrt{\frac{1}{4} + 2D\ {\xi_{ab}^0}^2}. \tag{17}$$

The normalization factor assumes integration on dQ over $]-\xi_{ab}^0, +\infty[$.

For H_2 in its GS, a reasonable set of parameters would be $\lambda = 36.7734$ au and $\xi_{ab}^0 = 42.4422$ au. Given $\mu_{ab} = \frac{m_H}{2} = 918.576$ au, one gets $D = 0.365148$ hartree, not really close to the dissociation energy $D_e = 0.166107$ hartree. However, with these parameters the zero point energy is, $D - E_0 = 2179.31$ cm^{-1} , as obtained from spectroscopic analysis [37].

Given this choice of wave function, the integrals over Q in Eq.(14) are calculated to be,

$$\langle\phi_0^{(0)}(Q)| - \frac{1}{2}\Delta_Q|\phi_0^{(0)}(Q)\rangle_Q = \frac{(\lambda-1)^2}{2\,(2\lambda-1)\ {\xi_{ab}^0}^2} \tag{18}$$

$$\langle\phi_0^{(0)}(Q)|\frac{\sqrt{\mu_{ab}}Z_aZ_b}{|\xi_{ab}^0+Q|}|\phi_0^{(0)}(Q)\rangle_Q = \frac{(\lambda-1)\sqrt{\mu_{ab}}Z_aZ_b}{\lambda\ \xi_{ab}^0}, \tag{19}$$

which shows that the nuclear repulsion energy is damped by a factor $\frac{\lambda-1}{\lambda}$ by convolution with nuclear motion. Note that considering rotational motion would just add an additional constant, $\langle\phi_0^{(0)}(Q)|\frac{\mu_{ab}J(J+1)}{|\xi_{ab}^0+Q|^2}|\phi_0^{(0)}(Q)\rangle_Q$ to Eq.(14). These matrix elements can be calculated analytically for a general wave function, Eq.(15), with the help of the formulas of Ref. [36], implemented in the code CONVIV [14,38].

So, coming back to the H_2 example and $J = 0$, the constant in Eq.(14) would be about 0.699578 au.

It remains to evaluate the last two symmetrical one-electron integrals of Eq.(14), which gives an effective attractive potential for the electrons. However, in practice this potential, which corresponds to an attractive Coulomb potential convoluted with nuclear motion, needs not be calculated explicitly. One only needs to calculate matrix elements between pairs of one-electron orbital basis functions of the form,

$$I_{e-n}[Z_I, r_{I_z}^0, \eta] = \langle\phi_0^{(0)}(Q)\chi_1(\vec{r^e})|\frac{Z_I}{\sqrt{(r_x^e)^2+(r_y^e)^2+(r_z^e-r_{I_z}^0+\eta Q)^2}}|\phi_0^{(0)}(Q)\chi_2(\vec{r^e})\rangle. \tag{20}$$

We will consider the case of primitive Gaussian functions

$$\chi_i(\vec{r^e}) = N_i(r_x^e)^{l_i}(r_y^e)^{k_i}(r_z^e-r_{i_z}^0)^{j_i}Exp\left[-\zeta_i\left((r_x^e)^2+(r_y^e)^2+(r_z^e-r_{i_z}^0)^2\right)\right], \tag{21}$$

where N_i is a normalization factor. Then, setting,

$$I_{e-n}[Z_I, r_{I_z}^0, \eta] = \frac{Z_I N_1 N_2\left[2(\lambda-1)\right]^{2\lambda+1}}{\Gamma[2\lambda+1]}\tilde{I}_{e-n}[r_{I_z}^0+\eta\xi_{ab}^0, \eta\xi_{ab}^0] \tag{22}$$

we have to calculate,

$$
\begin{aligned}
\tilde{I}_{e-n}[\tilde{r}^0_{I_z},\tilde{\eta}] &= \int_0^{+\infty} d\alpha\ \alpha^{2\lambda} Exp\left[2(1-\lambda)\alpha\right] \int_{-\infty}^{+\infty} dr^e_x \int_{-\infty}^{+\infty} dr^e_y \int_{-\infty}^{+\infty} dr^e_z \\
&\times Exp\left[-(\zeta_1+\zeta_2)(r^e_x)^2\right] Exp\left[-(\zeta_1+\zeta_2)(r^e_y)^2\right] Exp\left[-\zeta_1(r^e_z-r^0_{1_z})^2-\zeta_2(r^e_z-r^0_{2_z})^2\right] \\
&\times \frac{(r^e_x)^{l_1+l_2}(r^e_y)^{k_1+k_2}(r^e_z-r^0_{1_z})^{j_1}(r^e_z-r^0_{2_z})^{j_2}}{\sqrt{(r^e_x)^2+(r^e_y)^2+(r^e_z-\tilde{r}^0_{I_z}+\tilde{\eta}\alpha)^2}} \\
&= \int_0^{+\infty} d\alpha\ \alpha^{2\lambda} Exp\left[2(1-\lambda)\alpha\right] \int_0^{+\infty} \frac{d\beta}{\sqrt{\pi\beta}} \int_{-\infty}^{+\infty} dr^e_x (r^e_x)^{l_1+l_2} Exp\left[-(\zeta_1+\zeta_2+\beta)(r^e_x)^2\right] \\
&\times \int_{-\infty}^{+\infty} dr^e_y (r^e_y)^{k_1+k_2} Exp\left[-(\zeta_1+\zeta_2+\beta)(r^e_y)^2\right] \int_{-\infty}^{+\infty} dr^e_z (r^e_z-r^0_{1_z})^{j_1}(r^e_z-r^0_{2_z})^{j_2} \\
&\times Exp\left[-\zeta_1(r^e_z-r^0_{1_z})^2-\zeta_2(r^e_z-r^0_{2_z})^2-\beta(r^e_z-\tilde{r}^0_{I_z}+\tilde{\eta}\alpha)^2\right] \\
&= \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}}\Gamma\left[\frac{k_1+k_2+1}{2}\right]\Gamma\left[\frac{l_1+l_2+1}{2}\right] Exp\left[-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z}-r^0_{2_z})^2\right] \\
&\times \int_0^{+\infty} d\alpha\ \alpha^{2\lambda} Exp\left[2(1-\lambda)\alpha\right] \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1+\zeta_2+\beta)^{-\frac{k_1+k_2+l_1+l_2}{2}-1} \\
&\times Exp\left[-\frac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\frac{\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2}-\tilde{r}^0_{I_z}+\tilde{\eta}\alpha\right)^2\right] \\
&\int_{-\infty}^{+\infty} dr^e_z (r^e_z-r^0_{1_z})^{j_1}(r^e_z-r^0_{2_z})^{j_2} Exp\left[-\left(\zeta_1+\zeta_2+\beta)(r^e_z-\frac{\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)}{\zeta_1+\zeta_2+\beta}\right)^2\right] \\
&= \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}}\Gamma\left[\frac{k_1+k_2+1}{2}\right]\Gamma\left[\frac{l_1+l_2+1}{2}\right] Exp\left[-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z}-r^0_{2_z})^2\right] \\
&\times \sum_{i_1=0}^{j_1}\sum_{i_2=0}^{j_2}(-1)^{j_1+j_2-i_1-i_2}\frac{j_1!j_2!(r^0_{1_z})^{j_1-i_1}(r^0_{2_z})^{j_2-i_2}}{i_1!i_2!(j_1-i_1)!(j_2-i_2)!}\delta^{[2]}_{0,i_1+i_2}\Gamma\left[\frac{i_1+i_2+1}{2}\right] \\
&\times \int_0^{+\infty} d\alpha\ \alpha^{2\lambda} Exp\left[2(1-\lambda)\alpha\right] \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1+\zeta_2+\beta)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+3}{2}} \\
&\times Exp\left[-\frac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\frac{\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2}-\tilde{r}^0_{I_z}+\tilde{\eta}\alpha\right)^2\right], \qquad (23)
\end{aligned}
$$

where $\delta^{[2]}_{0,k}$ is 0 or 1 according to k being odd or even. Let us consider first the integral over β,

$$
\begin{aligned}
I_\beta[i_1,i_2,\alpha] &= \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1+\zeta_2+\beta)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+3}{2}} \\
&\times Exp\left[-\frac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\frac{\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2}-\tilde{r}^0_{I_z}+\tilde{\eta}\alpha\right)^2\right], \qquad (24)
\end{aligned}
$$

and make the change of variable $\beta \to \gamma = \frac{\beta}{\zeta_1+\zeta_2+\beta}$,

$$I_\beta[i_1,i_2,\alpha] = (\zeta_1+\zeta_2)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}} \int_0^{+1} d\gamma\ \gamma^{-\frac{1}{2}}(1-\gamma)^{+\frac{k_1+k_2+l_1+l_2+i_1+i_2}{2}} \times Exp\left[-\frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\ \gamma\right], \tag{25}$$

where we recognize the confluent hypergeometric function ${}_1F_1[a,c;x]$ [39],

$$I_\beta[i_1,i_2,\alpha] = (\zeta_1+\zeta_2)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}} \frac{\Gamma[\frac{1}{2}]\Gamma[\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}]}{\Gamma[\frac{k_1+k_2+l_1+l_2+i_1+i_2+3}{2}]} \times {}_1F_1\left[\frac{1}{2},\frac{k_1+k_2+l_1+l_2+i_1+i_2+3}{2};-\frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\right]. \tag{26}$$

However, it is probably more practical to integrate numerically using Rys quadrature after a new change of variable, $\gamma \to \tau = \sqrt{\gamma}$,

$$I_\beta[i_1,i_2,\alpha] = 2(\zeta_1+\zeta_2)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}} \int_0^{+1} d\tau\ (1-\tau^2)^{\frac{k_1+k_2+l_1+l_2+i_1+i_2}{2}} \times Exp\left[-\frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\ \tau^2\right]. \tag{27}$$

the $\delta^{[2]}$ functions in Eq.(23) insure that the Rys quadrature will be exact, since $\frac{k_1+k_2+l_1+l_2+i_1+i_2}{2}$ will always be an integer. The minimum number of quadrature points or "roots" to have an exact quadrature, is the smallest integer larger than half the degree of the polynomial in factor of the Gaussian functions, that is to say, in the present case:

$$n^{\text{Rys}}_{\text{roots}} = \frac{k_1+k_2+l_1+l_2+i_1+i_2}{2}. \tag{28}$$

So, setting,

$$\nu(\alpha) = \frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}, \tag{29}$$

we can rewrite exactly $I_\beta[i_1,i_2,\alpha]$ as a discretized Rys sum:

$$I_\beta[i_1,i_2,\alpha] = 2(\zeta_1+\zeta_2)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}} \sum_p w^{\text{Rys}}_p[\nu(\alpha)](1-\tau_p[\nu(\alpha)]^2)^{\frac{k_1+k_2+l_1+l_2+i_1+i_2}{2}} \tag{30}$$

where the $\tau_p[\nu(\alpha)]$'s are the roots of the Rys polynomials, and $w_p^{\mathrm{Rys}}[\nu(\alpha)]$'s the Rys "weights". Clearly, this can only be evaluated for a finite set of α-values. So, the integral over α has to be integrated numerically too, and Laguerre-Gauss quadrature seems the most appropriate scheme:

$$\begin{aligned}\tilde{I}_{e-n}[\tilde{r}^0_{I_z},\tilde{\eta}] &= \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}}\Gamma\left[\frac{k_1+k_2+1}{2}\right]\Gamma\left[\frac{l_1+l_2+1}{2}\right]Exp\left[-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z}-r^0_{2_z})^2\right]\\ &\times\sum_{i_1=0}^{j_1}\sum_{i_2=0}^{j_2}(-1)^{j_1+j_2}\frac{j_1!j_2!(r^0_{1_z})^{j_1-i_1}(r^0_{2_z})^{j_2-i_2}}{i_1!i_2!(j_1-i_1)!(j_2-i_2)!}\delta^{[2]}_{0,i_1+i_2}\Gamma\left[\frac{i_1+i_2+1}{2}\right]\frac{2(\zeta_1+\zeta_2)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}}}{[2(\lambda-1)]^{2\lambda+1}}\\ &\times\sum_p\sum_q w_q^{\mathrm{Lag}}w_p^{\mathrm{Rys}}[\nu(\frac{\kappa_q}{2(\lambda-1)})]\kappa_q^{2\lambda}(1-\tau_p[\nu(\frac{\kappa_q}{2(\lambda-1)})]^2)^{\frac{k_1+k_2+l_1+l_2+i_1+i_2}{2}},\end{aligned}\tag{31}$$

where κ_q are Laguerre polynomials roots and w_q^{Lag} Laguerre-Gauss weight.

Inserting Eq.(31) into Eq.(22) gives the required integrals for performing an electronic calculation, in the MF of the vibrational dof GS. (Electron kinetic energy and electron repulsion integrals are already calculated in all quantum chemistry package). Solving the eigenvalue problem for the Hamiltonian of Eq.(14), one obtains a wave function $\phi^{(1)}_{\vec{0}}(\vec{R}^e)$ which can be used in Eq.(13) to obtain a new MF Hamiltonian for the vibration dof. The derivation of the integrals required follows the same pattern, in particular the electron-vibration coupling integrals can be obtained by quadrature, between pairs of possibly excited Kratzer basis functions. The only real complication will be the evaluation of confluent hypergeometric functions at quadrature points. Then, performing a CI for the new MF vibrational Hamiltonian, a basis set $\phi^{(2)}_k(Q)$ will be obtained. One can iterate this process or decide to diagonalize the total Hamiltonian in a possibly truncated, product basis $\phi^{(1)}_{\vec{K}}(\vec{R}^e)\otimes\phi^{(2)}_k(Q)$. The only unusual integrals required to compute Hamiltonian matrix elements are those of the coupling term, Eq.(6), and we have seen, how to deal with them with the double quadrature method.

4 Conclusion

The EN-GMFCI approach remedy to the drawbacks encountered in previous endeavour to treat electrons and nuclei on an equal footing. First, the basis sets used to describe the vibrational states are expressed in terms of appropriate vibrational basis functions, as used in vibrational codes. This avoids the shortcomings of the Gaussian basis sets with limited angular quantum number values used in NOMO or NEO codes.

Second, the EN-GMFCI method only couples the electronic and nuclear degrees of freedom in a CI calculation after having obtained properly correlated vibrational and electronic wave functions. So the crucial GMFCI step contracting all dof has mainly to deal with electron-vibration correlation. Of course, the purely electronic and purely vibrational correlations are affected too, because the Hamiltonian in the last GMFCI step is the full Hamiltonian and not partial mean field Hamiltonians that have served to obtain the correlated basis functions. However, the partial general mean field Hamiltonian can be realistic enough to capture the dominant purely electronic and purely vibrational correlations.

The energy expression for diatomic EN-GMFCI calculations limited to a one-dimensional vibrational nuclear dof has been fully worked out. Dealing with rotational dof adds no particular difficulty in the diatomic case. However, dealing with more nuclear dofs will result in integrals being not separable in the general case. One will have to use numerical techniques as already developed for purely ro-vibrational calculations [40,41].

However, the method is general and not limited to the special form of Hamiltonian used in this article. Other general curvilinear coordinates can be used to describe nuclear motion, and the terms neglected such as mass polarization terms, coupling terms between electronic angular momentum and total angular momentum can in principle be taken into account, we just wanted here to expose the principle of the method avoiding unnecessary technical complications.

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References

[1] M. Born and J. R. Oppenheimer, Ann. der Phys. 84 (1927) 457.

[2] A. Fröman, J. Chem. Phys 36 (1962) 1490. (earlier preprint contains much more information than the printed version)

[3] B. Sutcliffe, J. Math. Chem. 44 (2008) 988.

[4] P. Cassam-Chenaï, Chem. Phys. Lett. 420 (2006) 354-357.

[5] M. Tachikawa, K. Mori, K. Suzuki, K. Iguchi, Int. J. Quantum Chem. 70 (1998) 491.

[6] M. Tachikawa, Y. Osamura, Theor. Chim. Acta. 104 (2000) 29.

[7] H. Nakai, K. Sodeyama, M. Hoshino, Chem. Phys. Lett. 345 (2001) 118.

[8] Y. Shigeta, Y. Ozaki, K. Kodama, H. Nagao, H. Kawabe, K. Nishikawa, Int. J. Quantum Chem. 69 (1998) 629.

[9] S. P. Webb, T. Iordanov, and S. Hammes-Schiffer, J. Chem. Phys 117 (2002) 4106.

[10] M. Cafiero and L. Adamowicz, Chem. Phys. Lett. 387 (2004) 136.

[11] E. Matyus and M. Reiher, J. Chem. Phys 135 (2011) 204302.

[12] P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. 93 (2003) 245-264.

[13] P. Cassam-Chenaï, J. Chem. Phys 124 (2006) 194109-194123.

[14] P. Cassam-Chenaï, J. Liévin, Journal of Computational Chemistry 27 (2006) 627-640.

[15] P. Cassam-Chenaï, A. Ilmane, J. Math. Chem. 50 (2012) 652-667.

[16] P. Cassam-Chenaï, http://hal-unice.archives-ouvertes.fr/hal-00785488

[17] H. F. King, M. Dupuis, J. Chem. Phys 65 (1976) 111.

[18] H. F. King, M. Dupuis, J. Comp. Phys. 21 (1976) 144.

[19] R. P. Sagar, V. H. Smith Jr., Int. J. Quantum Chem. 42 (1992) 827.

[20] P. Cassam-Chenaï, D. Jayatilaka, J. Chem. Phys 137 (2012) 064107.

[21] C. Eckart, Phys. Rev. 47 (1935) 552.

[22] B. Sutcliffe, Theor. Chim. Acta. 127 (2010) 121.

[23] B. Sutcliffe, Theor. Chim. Acta. 130 (2011) 187.

[24] B. Sutcliffe, Theor. Chim. Acta. 131 (2012) 1215.

[25] J. K. G. Watson, Mol. Phys. 15 (1968) 479-490.

[26] J. K. G. Watson, Mol. Phys. 19 (1970) 465-487.

[27] P. R. Bunker and R. E. Moss, Mol. Phys. 33 (1977) 417.

[28] D. R. Hartree, Proc. Cambridge Phil. Soc. 24 (1928) 89.

[29] J. C. Slater, Phys. Rev. 34 (1929) 1293.

[30] J. C. Slater, Phys. Rev. 35 (1930) 210.

[31] V. Fock, Z. Physik 61 (1930) 126.

[32] E. A. Hylleraas, Z. Physik 54 (1929) 347.

[33] P. Cassam-Chenaï, G. Granucci Chem. Phys. Lett. 450 (2007) 151-155.

[34] P. Cassam-Chenaï, V. Rassolov, Chem. Phys. Lett. 487 (2010) 147-152.

[35] A. Kratzer, Z. Physik 3,(1920) 289

[36] Don Secrest, J. Chem. Phys 89 (1988) 1017.

[37] K. K. Irikura, J. Phys. Chem. Ref. Data 36 (2007) 389.

[38] https://forge.oca.eu/trac/conviv

[39] Bateman Manuscript Project, "Higher Transcendental Functions", (Erdlyi, A., Ed.; McGraw-Hill: New York, 1953).

[40] E. Mátyus, J. Šimunek, A. G. Császár, J. Chem. Phys 131 (2009) 074106.

[41] X.-G. Wang, T. Carrington, J. Chem. Phys 138 (2013) 104106.