Decoupling electrons and nuclei without the Born-Oppenheimer approximation

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Decoupling electrons and nuclei without the Born-Oppenheimer approximation: The Electron-Nuclei Mean-Field Configuration Interaction Method

Patrick Cassam-Chenaï[1, a)] and Bingbing Suo, Wenjian Liu[2, b)]

[1)] *Univ. Nice Sophia Antipolis, CNRS, LJAD, UMR 7351, 06100 Nice, France.*

[2)] *Beijing National Laboratory for Molecular Sciences, Institute of Theoretical and Computational Chemistry, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, and Center for Computational Science and Engineering, Peking University, Beijing 100871, People's Republic of China*

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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 problems of these Hamiltonians are solved in basis sets giving partial eigensolutions for the active degrees of freedom (dof's), that is to say, either for the electrons or for nuclear motion. The process can be iterated or electron and nuclear motion dof's can be contracted in a CI calculation. In the EN-GMFCI reduction of the molecular Schrödinger equation to an electronic and a nuclear problem, the electronic wave functions do not depend parametrically upon nuclear coordinates. So, it is different from traditional adiabatic methods. Furthermore, when contracting electronic and nuclear functions, a direct product basis set is built in contrast with methods which treat electron and nuclei on the same footing, but where electron-nucleus explicitly correlated coordinates are used. Also, the EN-GMFCI approach can make use of the partition of molecular dof's into translational, rotational and internal dof's. As a result, there is no need to eliminate translations and rotations from the calculation, and the convergence of vibrational levels is facilitated by the use of appropriate internal coordinates. The method is illustrated on diatomic molecules.

[a]Electronic mail: cassam@unice.fr

[b]Electronic mail: liuwjbdf@gmail.com

I. 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] (see however[4] for a review of new mathematical results). 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[5]. The number of points needed to described accurately a full-dimensional PES grows exponentially 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 addressed 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...

Among all these problems, the most serious one hit in practice, is arguably the curse of dimensionality: the exponential growth of grid points with the number of internal degrees of freedom (dof). It has been proposed to tame this numerical scaling by limiting PES descriptions to only few mode couplings. However, as the number of dof increases the probability of accidental resonances between larger and larger numbers of dof's also increases. When such resonances occur, calculations become very sensitive to the high order intermode coupling constants of the dof's involved, even though the mechanical coupling between them might be quantitatively small.

The purpose of the present article is to show that the construction of a BO PES can be bypassed and that one can obtain simultaneously accurate electronic and vibrational energy levels in a single calculation using a direct product basis set, that is to say with electronic basis functions independent of nuclear coordinates. This makes our proposal fundamentally different from the non-adiabatic approaches briefly recalled below.

A simple idea to go beyond the BO approach consists in coupling different BO electronic states. This is limited to small systems and a reduced number of electronic states, since it requires the computation of one PES per electronic state plus their coupling element surfaces (see Ref.[6] for example). In practice, one can use test functions instead of approximate solutions of the adiabatic eigenvalue equation[7,8]. A different approach is the generator coordinate approach, which instead of dealing with different electronic states, uses one electronic function parametrized by so-called "generator coordinates"[9]. New proposals have appeared recently either for the time independent Schrödinger equation, such as the free complement method[10,11], a revival of Hunter's factorized wave function[12], or in a time dependent context such as the multi-configuration electron-nuclear dynamics method (MCEND)[13], a time-dependent version of Hunter's factorized wave function[14–17]. More time will be needed to fully evaluate these new approaches, however they show that this field of research is vividly active.

Thomas was a precursor in treating electrons and H-nuclei simultaneously with an orbital method[18], but he was dealing only with specific problems such as the ammonia molecule. Several groups worldwide have developed wave function methods dealing on an equal footing with electron and nuclei degrees of freedom. There is essentially one and the same idea developed under different names by different groups:

- The FVMO (full variational treatment of molecular orbital) method of Tachikawa et al.[19,20], is a one-particle self-consistent field (SCF) method with simultaneous optimization of Gaussian exponents and centers performed analytically (note that such exponents and centers optimisation has also been performed in Ref.[21] but numerically). Later, the method was renamed, DEMO (dynamic extended molecular orbital) method[22], then called NOMO (nuclear orbital molecular orbital) by Nakai et al.[23] and extended to configuration interaction (CI), Coupled Cluster (CC) and perturbative post-treatments[24,25], see Ref.[26] for a review. Another name is yet MCMO (multi-component molecular orbital) method often used when it is combined with the fragment molecular orbital (FMO) method[27];
- The CMFT-GCM (coupled mean-field theory- generator coordinate method) of Shigeta et al.[28] who later turned towards non-BO DFT;

- The NEO (nuclear-electronic orbital) method and its declension into Hartree-Fock (NEO-HF), CI (NEO-CI), multi-configuration SCF (NEO-MCSCF) and perturbative variants[31–33].
- The ENMO (electronic and nuclear molecular orbital) approaches with different level of correlation treatments from none (SCF) to Möller-Plesset perturbation theory (MBPT) and CI[36].
- The APMO (any particule molecular orbital) method[34] extended to MP2 in Ref.[35]. A review of its further developments can be found in Ref.[37].

In their original formulations, these approaches usually start from a global single product wave function for all degrees of freedom. That is to say, they have to recover electronic correlation, nuclear correlation and electron-nucleus correlation in the post-treatment. More recently, the specific difficulties to treat electron-nucleus correlation have led several authors[38–41] to introduce explicitly correlated geminal Gaussian basis function, inspired by the pioneering work of Cafiero and Adamowicz[42,43] and/or Suzuki and Varga[44]. Note that similar ideas have appeared in a time-dependent context[45]. However, the explicitly correlated ansatz reintroduce nuclear variables in the electronic wave function, as in the BO framework, with significant consequences for the computational cost.

So far, in our opinion, the success of most of these methods has been limited by the computational cost due to the use of explicitly correlated basis sets and/or because the coordinates were not appropriate to describe vibrational motion. In the latter case, the basis sets used for the nuclear degrees of freedom were not amenable to describe sufficiently excited vibrational states. Moreover, translational and rotational energy contributions can contaminate the calculation of vibrational frequencies[23,26]. These drawbacks can be easily avoided with a MFCI approach[46–49].

The MFCI method is a general approach that has proved very effective to solve the vibrational Schrödinger equation[46,48]. 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[50], giving increased flexibility: the so-called "GMFCI" method.

Here, we propose to generalize the GMFCI ideas to a set of both electrons and nuclei. The main difference is that we have to relax the constraint on the Hamiltonian to be a sum of products of separable contraction operators. Rotational dof will be omitted to simplify the presentation, although they can be included in a similar fashion as vibrational dof's. This issue will be discussed in conclusion. In the diatomic case, rotational levels can and will be calculated in a straitforward manner. First, we will obtain a basis set of electronic wave functions by diagonalizing a mean field electronic Hamiltonian. The latter will only require a realistic zero order fundamental vibratonal wave function. If this function is a Dirac distribution centered at a given nuclear geometry, the BO electronic Hamiltonian will be recovered. Then, we will be able to obtain a basis set of vibrational wave functions by diagonalizing a mean field vibrational Hamiltonian. The latter will not require a BO PES as in the traditional approach but a mean field PES corresponding to an electronic wave function obtained at the previous step.

Such a mean field PES has been investigated in a time dependent context[45]. It is physically correct near the equilibrium geometry, but qualitatively incorrect away from this geometry, in particular, at long distance where no dissociation occurs. Such a behaviour is expected and turns out to be an advantage in our approach, since it allows us to obtain basis sets of vibrational functions of arbitrary sizes, to be combined with electronic basis functions in a product basis set. Would the PES curve dissociates, only a limited set of bounded vibrational basis functions could be obtained by solving the mean-field vibrational Schrödinger equation, and it is likely that, for some systems the resulting electron-vibration product basis set would not be sufficiently large to describe accurately the eigenstates of the total electron-nuclei problem.

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. We will show in Appendix that double Rys quadrature[51–54] combined with generalized Gauss-Laguerre quadrature, is a practical way to calculate the required integrals, when Kratzer oscillator basis functions are used to describe the vibratonal wave functions. Only these integrals among those required to perform a contraction of vibrational and electronic dof's, are of a new type not already implemented in widely-distributed quantum chemistry codes.

The article is organized as follows: First the general frame of the GMFCI method for electrons and nuclei is presented. Next, we explain how are computed the integrals required for the Hamiltonian matrix element evaluations, leaving the essential but more technical details in Appendix A. Then, we present some application and convergence studies on dihydrogen isotopologues. Finally, we conclude on the prospects of the method.

II. 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 in many cases. When this is so, it makes sense physically to consider them independently in the mean field of the others in first approximation. Then, if such a mean field approximation proves too rough, one can couple some dof's to refine the description.

A. 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[55] 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[3,56]. 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 non-diagonal mass-polarization terms and reduced-mass corrections that are neglected here. The separation of rotational motion from electronic dofs also imposes the neglect of terms involving the electronic angular momenta[57,58]. The full rovibrational Eckart-Watson Hamiltonian[55,59,60] could have been introduced, however, in the present section, rotational dof's and Coriolis couplings are omitted to simplify the presentation. They will be considered in the last sections of this article.

B. 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

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

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,

$$
\hat{H}^{cn}(\vec{R^e}) = -\tfrac{1}{2}\sum_{i=1}^{p}\Delta_{\vec{r}_i^e} + \sum_{1\leq i<j\leq p}\frac{1}{\|\vec{r_i}^e-\vec{r_j}^e\|} - \sum_{i=1}^{p}\sum_{a=1}^{N}\frac{Z_a}{\|\vec{r_i}^e-\vec{r_a}^0\|} + \sum_{1\leq a<b\leq N}\frac{Z_aZ_b}{\|\vec{r_a}^0-\vec{r_b}^0\|}.
\tag{8}
$$

Alternatively, one can choose $\phi_{\vec{0}}^{(0)}(\vec{Q}) = \bigotimes_{i=1}^{q}\phi_0^i(Q_i)$, that is to say, a product of GS eigenfunctions of some one-dimensional model Hamiltonians, as a guess to initiate the EN-GMFCI process. Then, one notices that nuclear cusps are smeared off in the Hamiltonian Eq.(7), and related basis set convergence issues may be removed[37]. Also, approximate excited states represented by products of k_i^{th}-excited functions, $\phi_{\vec{K}}^{(0)}(\vec{Q}) = \bigotimes_{i=1}^{q}\phi_{k_i}^i(Q_i)$, with $\vec{K} = (k_1,\ldots,k_q)$, can be used to build a more general MF Hamiltonian, for instance, a second order GMF Hamiltonian[50] (setting $\vec{0} := (0,\cdots,0)$),

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

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, valid for non-degenerate GS, is reminiscent of that of Bunker and Moss[61] obtained by contact transformation, which account for non adiabatic corrections to the electronic energy.

C. General Mean field Hamiltonian for the vibrational dof's

Assuming that a GMF Hamiltonian, Eq.(7), 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[62–65], configuration interaction[66], geminal-MFCI[47,67,68], 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,

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

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 eigenvalue of the effective Hamiltonian always corresponds to the total Hamiltonian expectation value of the wave function equal to the product of spectator GS wave functions (for example $\phi_{\vec{0}}^{(1)}(\vec{R}^e)$ in Eq.(10)) and of the (active) GS eigenfunction of $\hat{H}^{eff}(\vec{Q})$ (which can be denoted as $\phi_{\vec{0}}^{(2)}(\vec{Q})$ for the Hamiltonian of Eq.(10)). 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[48,49].

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. To have a description of electron-nuclei correlation, one has to contract electronic and vibrational dof's and perform a CI calculation on the whole system.

III. INTEGRAL CALCULATIONS

A. 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 $\xi^0_{ab} = \|\sqrt{\mu_{ab}}(\vec{r}_a^{\,0} - \vec{r}_b^{\,0})\|$, (by convention the z-axis is oriented such that $r_{a_z} \geq r_{b_z}$). 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,

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

and Eq. (7) becomes,

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

Let us begin with 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 (second term on the left-hand side of Eq. (13)) integrals will diverge. So, we choose a Kratzer potential basis set, which is not only more accurate but also leads to 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, $D\left(\frac{Q}{Q+\xi_{ab}^0}\right)^2$[69,70]. However, to initiate the MFCI process, this expansion will be limited to the term $i = 0$,

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

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 $\lambda = 36.754020$ au and $\xi_{ab}^0 = 42.430690$ au. Given $\mu_{ab} = \frac{m_H}{2} = 918.07633622$ au, one gets $D = .364955$ hartree, not really close to the dissociation energy $D_e = 0.166107$ hartree. However, with these parameters the zero point energy is, 2179.31 cm^{-1} , as obtained from spectroscopic analysis[72]. The same values of D and of the equilibrium distance (parameters specifying the Kratzer potential required as input in our code) will be used for all isotopologues. The corresponding values of λ and ξ_{ab}^0 are displayed in Tab. I.

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, $\langle\phi_0^{(0)}(Q)|\frac{J(J+1)}{2|\xi_{ab}^0+Q|^2}|\phi_0^{(0)}(Q)\rangle_Q$ to Eq.(14). These matrix elements, as well as general ones between arbitrary Kratzer basis functions needed for a general wave function, Eq.(15), can be calculated analytically with the help of the formulas of Ref.[70], implemented in the code CONVIV[48,73].

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,

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

where, $\eta = -\frac{\sqrt{\mu_{ab}}}{m_a}$ or $\eta = +\frac{\sqrt{\mu_{ab}}}{m_b}$.

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, setting $\tilde{r}_{I_z}^0 = r_{I_z}^0+\eta\xi_{ab}^0,\ \tilde{\eta} = \eta\xi_{ab}^0,\ \alpha = \left(1+\frac{Q}{\xi_{ab}^0}\right)$,

$$\begin{aligned}\tilde{I}_{e-n}[\tilde{r}_{I_z}^0, \tilde{\eta}] &= \int_0^{+\infty} d\alpha\ \alpha^{2\lambda}Exp\left[2(1-\lambda)\alpha\right]\int_{-\infty}^{+\infty}dr_x^e\int_{-\infty}^{+\infty}dr_y^e\int_{-\infty}^{+\infty}dr_z^e\\ &\times Exp\left[-(\zeta_1+\zeta_2)(r_x^e)^2\right]Exp\left[-(\zeta_1+\zeta_2)(r_y^e)^2\right]Exp\left[-\zeta_1(r_z^e-r_{1_z}^0)^2-\zeta_2(r_z^e-r_{2_z}^0)^2\right]\\ &\times\frac{(r_x^e)^{l_1+l_2}(r_y^e)^{k_1+k_2}(r_z^e-r_{1_z}^0)^{j_1}(r_z^e-r_{2_z}^0)^{j_2}}{\sqrt{(r_x^e)^2+(r_y^e)^2+(r_z^e-\tilde{r}_{I_z}^0+\tilde{\eta}\alpha)^2}}\end{aligned} \tag{23}$$

This is a particular case for two Kratzer GS basis functions of the general integral treated in Appendix A. Here, we only sketch the main steps of the derivation. A first intermediate step, consists in integrating over electronic variables,

$$\begin{aligned}\tilde{I}_{e-n}[\tilde{r}_{I_z}^0, \tilde{\eta}] &= \frac{\delta_{0,k_1+k_2}^{[2]}\delta_{0,l_1+l_2}^{[2]}}{\sqrt{\pi}}\Gamma\left[\frac{k_1+k_2+1}{2}\right]\Gamma\left[\frac{l_1+l_2+1}{2}\right]Exp\left[-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r_{1_z}^0-r_{2_z}^0)^2\right]\\ &\times\sum_{i_1=0}^{j_1}\sum_{i_2=0}^{j_2}\binom{j_1}{i_1}\binom{j_2}{i_2}\delta_{0,i_1+i_2}^{[2]}\Gamma\left[\frac{i_1+i_2+1}{2}\right]\int_0^{+\infty}d\alpha\ \alpha^{2\lambda}Exp\left[2(1-\lambda)\alpha\right]I_\beta[i_1,i_2,\alpha],\end{aligned} \tag{24}$$

where $\delta^{[2]}_{0,k}$ is 0 or 1 according to k being odd or even, and,

$$I_\beta[i_1,i_2,\alpha] = \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1+\zeta_2+\beta)^{-\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2}} \left(\zeta_2(r^0_{2_z}-r^0_{1_z})+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{1_z})\right)^{j_1-i_1}$$
$$\times \left(\zeta_1(r^0_{1_z}-r^0_{2_z})+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{2_z})\right)^{j_2-i_2} Exp\left[-\frac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\frac{\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2}-\tilde{r}^0_{I_z}+\tilde{\eta}\alpha\right)^2\right]. \tag{25}$$

For $i_1=j_1$, (respectively, $i_2=j_2$), the undetermined factor $\left(\zeta_2(r^0_{2_z}-r^0_{1_z})+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{1_z})\right)^{j_1-i_1}$, (respectively, $\left(\zeta_1(r^0_{1_z}-r^0_{2_z})+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{2_z})\right)^{j_2-i_2}$), should be set to 1, when $\zeta_2(r^0_{2_z}-r^0_{1_z})+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{1_z})=0$, (respectively, $\zeta_1(r^0_{1_z}-r^0_{2_z})+\beta(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{2_z})=0$). The integral of Eq.(24) can be obtained analytically,

$$I_\beta[i_1,i_2,\alpha] = \sum_{s_1=0}^{j_1-i_1}\sum_{s_2=0}^{j_2-i_2}\binom{j_1-i_1}{s_1}\binom{j_2-i_2}{s_2}\zeta_1^{j_2-i_2-s_2}(-\zeta_2)^{j_1-i_1-s_1}(\zeta_1+\zeta_2)^{s_1+s_2-\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-1}$$
$$\times (r^0_{1_z}-r^0_{2_z})^{j_1+j_2-i_1-i_2-s_1-s_2}(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{1_z})^{s_1}(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha-r^0_{2_z})^{s_2} I_\gamma[s_1,s_2,\alpha], \tag{26}$$

where, $I_\gamma[s_1,s_2,\alpha]$ is related to the confluent hypergeometric function ${}_1F_1[a,c;x]$[74],

$$I_\gamma[s_1,s_2,\alpha] = \frac{\Gamma[s_1+s_2+\frac{1}{2}]\Gamma[\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-s_1-s_2+1]}{\Gamma[\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2}]}$$
$$\times\ {}_1F_1\left[s_1+s_2+\frac{1}{2},\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2};-\frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\right]. \tag{27}$$

However, it is more practical to calculate it numerically using Rys quadrature as explained in Appendix A. The $\delta^{[2]}$ functions in Eq.(24) insure that $\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}$ will always be an integer, and the Rys quadrature will be exact provided that the number of quadrature points is larger than this integer (see Appendix A). So, setting,

$$\nu(\alpha) = \frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}, \tag{28}$$

we can rewrite exactly $I_\gamma[s_1,s_2,\alpha]$ as a discretized Rys sum,

$$I_\gamma[s_1,s_2,\alpha] = 2\sum_p w^{\mathrm{Rys}}_p[\nu(\alpha)]\tau_p[\nu(\alpha)]^{2(s_1+s_2)}(1-\tau_p[\nu(\alpha)]^2)^{\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-s_1-s_2}, \tag{29}$$

where the $\tau_p[\nu(\alpha)]$'s are the roots of the Rys polynomials, and $w^{\mathrm{Rys}}_p[\nu(\alpha)]$'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 generalized Gauss-Laguerre quadrature seems the most appropriate scheme[75]:

$$\tilde{I}_{e-n}[\tilde{r}^0_{I_z},\tilde{\eta}] = \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}}\Gamma\left[\frac{k_1+k_2+1}{2}\right]\Gamma\left[\frac{l_1+l_2+1}{2}\right] Exp\left[-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z}-r^0_{2_z})^2\right]$$
$$\times\sum_{i_1=0}^{j_1}\sum_{i_2=0}^{j_2}\binom{j_1}{i_1}\binom{j_2}{i_2}\delta^{[2]}_{0,i_1+i_2}\Gamma\left[\frac{i_1+i_2+1}{2}\right]\sum_q w_q^{\mathrm{Lag}} I_\beta[i_1,i_2,\kappa_q], \tag{30}$$

where κ_q and w_q^{Lag} are respectively the generalized Gauss-Laguerre polynomials roots and weights corresponding to parameters $(2\lambda, 2(\lambda-1))$.

Inserting Eq.(30) into Eq.(22) gives the required integrals for performing an electronic calculation, in the MF of the vibrational dof's GS, electron kinetic energy and electron repulsion integrals being already available 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's. 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 Appendix A explains how to deal with them with the double quadrature method. The integrals have been implemented in the BDF code[76–79] and thoroughly checked against a Mathematica[80] code.

B. Generalization to larger polyatomics

We have seen in the diatomic case, that the electron-nucleus attraction integrals could be dealt with by quadrature integration. In the polyatomic case, the same techniques can be applied:

- The expression $\frac{Z_a}{\|\vec{r}_i{}^e-\vec{r}_a{}^0-\hat{G}_a^{-1}\hat{L}^T\vec{Q}\|}$ can be cast into an exponential form using the Laplace formula

$$\frac{1}{\|\vec{r}_i^{\,e} - \vec{r}_a^{\,0} - \hat{G}_a^{-1}\hat{L}^T\vec{Q}\|} = \frac{1}{\sqrt{\pi}}\int_0^{+\infty} Exp\left[-v\|\vec{r}_i^{\,e} - \vec{r}_a^{\,0} - \hat{G}_a^{-1}\hat{L}^T\vec{Q}\|^2\right]\frac{dv}{\sqrt{v}} \qquad (31)$$

- The integrals over the three electronic variables can be permuted with the Laplace integral and replaced by analytic expressions.

- The remaining integrals over the $(q+1)$ variables (i.e. the Laplace variable and the internal variables $(Q_i)_{i\in\{1,\cdots,q\}}$) can be performed numerically by the quasi Monte-Carlo quadrature integration of Ref.[81] for molecules up to penta-atomics. Smolyak's quadrature algorithm could also be considered, see Ref.[82] and therein. For larger systems, quasi Monte-Carlo techniques[83] achieve a speed of convergence for $(D = q+1)$-dimensional integrals, which scales as $O(\frac{ln[M]^q}{M})$, where M is the number of points.

The number of points can be reduced by more than one order of magnitude by calculating not directly the MFCI integrals, but their difference with respect to the corresponding traditional (i.e. those with cusps) integrals which can be efficiently obtained from quantum chemistry packages. Work in progress will be presented in a forthcoming article.

IV. RESULTS FOR DIHYDROGEN AND ISOTOPOLOGUES

The simplest non-trivial molecular systems to apply the EN-MFCI method is arguably dihydrogen and its isotopologues.

In the previous section, the so-called mass-polarization terms were neglected. They consist in two contributions: the diagonal contribution which amounts to the substitution of the electron mass by its reduced mass and the non-diagonal contribution which is a two-electron term coupling electron linear moments. In this section, for the sake of comparaison with reference calculations available in the literature[85–88], we include the diagonal contribution unless specified otherwise. For dihydrogen, it increases the ground state energy by about 70 cm^{-1} , as found in an adiabatic approach[91] for geometries close to equilibrium, and changes the fundamental frequency by only a few wave numbers. The non-diagonal contribution is expected to increase the ground state energy by about

6 cm^{-1} , if one assumes that the equilibrium value[91] is close to its vibrational ground state average, as for the diagonal contribution. It will be neglected for all isotopologues, since its effect on fundamental frequencies is expected to be less than 1 cm^{-1} .

So, the electronic kinetic terms in Eqs.(13) and (14) is replaced by $-\frac{1}{2\mu_e}\sum_{i=1}^{p}\Delta_{\vec{r_i^e}}$ where μ_e is the electronic reduced mass. Nuclear mass ratios were taken from NIST[96]: $\frac{m_p}{m_e} = 1836.15267244$, $\frac{m_d}{m_e} = 3670.48296514$, $\frac{m_t}{m_e} = 5496.92152668$. Therefore the electronic reduced masses in a frame fixed at the center of nuclear mass are $\mu_e = 0.999727765621\ m_e$ for H_2, $\mu_e = 0.999863796698\ m_e$ for D_2, $\mu_e = 0.999909048270\ m_e$ for T_2.

A. Basis set convergence

The first issue we need to address to carry out EN-MFCI calculations, is that of the choice of the basis set. The numerous electronic basis sets available in quantum chemistry packages have been tailored to describe static electronic densities in a clamped nuclei framework. Here, we need to described electronic densities spread out along all geometries accessible through vibrational motion. This is why we have added in an *ad hoc* manner, inner shell s-functions on both sides of standard H-nucleus electronic basis sets. The centers of all these basis functions are fixed, whatever the values of nuclear coordinates might be. So, the product basis set of electronic basis functions with the Kratzer basis functions used to describe nuclear motion, is a genuine direct product in the mathematical sense.

We have first examined the convergence of full CI calculation with the number of Kratzer basis functions, for two cc-pVTZ H-nucleus electronic basis sets[84] located apart from each other at approximately the H_2 GS equilibrium distance and different numbers of s-orbital pairs located on both sides of each cc-pVTZ H-nucleus basis center on the same axis, see Tab. II. The results suggest that the GS energies are converged to the μHartree precision with 16 Kratzer modal basis functions whatever the number of ghost atoms carrying 2s-basis sets might be. (Note that the H and Ghost atoms' electronic basis centers are fixed and independent of H-nucleus position variables.)

Looking at the GS energy variations as a function of the number of ghost atoms, n, in Tab. II, we see that a decrease of about 30 μHartree occurs when going from $n = 12$ to $n = 16$ whatever the number of Kratzer functions might be. This seems to be reduced to 11 μHartree for 16 Kratzer functions, when lowering the quasi-linear dependency cutoff from 10^{-6} to 10^{-7}, as seen from the third column of Tab. III. However, numerical accuracy issues prevented us to converge the cc-pVTZ calculation for $n = 16$. In the cc-pVDZ column, the difference is larger. This can be understood easily by the fact that the H-basis set being more incomplete, the importance of ghost atom basis sets is greater. On the other side, the cc-pVQZ, $n = 16$ energy is found higher than its $n = 12$ counterpart. This does not contradict the Hylleraas-Undheim-MacDonald theorem[92,93] since the variational spaces of the two calculations are not fully included one in the other, due to quasi-linear dependencies elimination. The $n = 16$ calculation has only 3 more orbitals than the $n = 12$ one and as a matter of fact among the 10 orbitals eliminated in the $n = 16$ calculation some were contributing to a few μHartree to the GS energy. This anomalous behaviour is not observed for the cc-pV5Z column, where a lowering of 7 μHartree is found between $n = 12$ and $n = 16$ calculations. This is less than the error due to the neglect of the off-diagonal mass-polarization (about 27 μHartree).

Examining now the convergence of GS energy with the number of valence orbitals in the H-atom correlation consistent polarized basis, we see in Tab. III, that there is still a 72 cm^{-1} difference between cc-pVQZ and cc-pV5Z. A sextuple zeta calculation appears necessary to improve convergence. It seems also necessary to obtain a fundamental frequency closer to the non relativistic result of Bubin et al.[86], see Tab. IV. The problem of finding adequate electronic basis sets for performing EN-MFCI calculation appears to be the most stringent one at present. The use of standard basis set is not appropriate, even large ones. The addition of off-centered or floating orbitals is probably not the end answer because of quasi-linear dependency issues and the numerical problems already discussed (*vide supra*). In the following of the paper, we have retained for the electronic basis set the one used in the last entries of Tabs. III and IV:

- Two sets of cc-pV5Z H-atom basis located 1.40036324 au apart
- 16 sets of 2s basis sets located on both sides of both cc-pV5Z H-atom basis with a step size of 0.08 au.

B. EN-SCF calculations

In the present study, we have limited ourselves to MF of order 1. So, iterating the same dof partition, i.e. the partition into vibrational and electronic dofs, the lowest eigenvalues of the successive effective Hamiltonians are the GS energies of the product wave functions $\phi_{\vec{0}}^{(0)}(\vec{Q})\phi_{\vec{0}}^{(1)}(\vec{R}^e), \cdots, \phi_{\vec{0}}^{(2n)}(\vec{Q})\phi_{\vec{0}}^{(2n+1)}(\vec{R}^e), \phi_{\vec{0}}^{(2n+2)}(\vec{Q})\phi_{\vec{0}}^{(2n+1)}(\vec{R}^e), \cdots$. If the effective Hamiltonians are solved variationally, and if for each dof subset (electron or vibrational coordinates) the successive variational spaces are kept identical (which we assume here) or possibly enlarged, the GS energy can only decrease iterations after iterations. The latter being bounded from below, the process ought to converge to a self-consistent solution. We call such a calculation an EN-SCF(V_{elec},V_{vib}) where V_{elec} (resp. V_{vib}) specifies the variational space for electrons (resp. vibrations).

Tab. V displays the convergence of two EN-SCF process with the iteration number corresponding to two different electronic variational spaces: the variational space explored by the Hartree-Fock method[94,95] and Full CI variational space. The effective vibrational Hamiltonian (even iteration numbers) is always solved by Full CI which amounts in this particular case to the diagonalization of the Hamiltonian in the space spanned by the 16 lowest eigenfunctions of the Kratzer model potential. In both cases, the ZPE is decreased by about 4 mHartree. This is one order of magnitude smaller than the decrease obtained by going from HF to Full CI. So, electron correlation is dominant. However, the EN-SCF lowering is not insignificant, and the optimization of the best (with respect to the energy lowering criterium) product wave function of the form $\phi_{\vec{0}}(\vec{Q})\phi_{\vec{0}}(\vec{R}^e)$, whether $\phi_{\vec{0}}(\vec{R}^e)$ is a HF or a Full CI wave function, is worth considering. In particular, if one wish to contract electrons and vibrations, one can think of selecting a subsets of the self-consistent electronic CI eigenfunctions (resp. vibrational CI eigenfunctions) to generate a product basis of reduced size but of good accuracy, as in VMFCI calculations[48].

C. Comparison with other methods

To assess the potential accuracy of our method, we have contracted electrons and vibration and performed Full electron-nucleus CI calculations. So, we have used all 16 Kratzer basis functions and step 1 electronic eigenfunctions to generate product functions, since without basis truncation all basis sets are equivalent, (in fact, we could have even used electronic configuration state functions instead of step 1 solutions).

First, we compare our vibrational and electronic energy differences with respect to NOMO results available in the literature[26], so the comparison is limited to the two lowest excited vibrational states and the lowest singlet excited state of the same symmetry as the GS, see Tab. VI. Clearly, our results are closer to the experimental results quoted in[26] in all cases. Even the translation-Free NOMO (TF-NOMO) Full CI fundamental frequencies of Tachikawa[99] are more than 10 cm^{-1} away for all isotopologues, whereas ours are within the cm^{-1} accuracy except for H_2.

Note that Webb et al.[31] reported a NEO-CI value for H_2 of 4161 cm^{-1} in perfect agreement with experiment. However, they admitted that, given the size of their basis, such an agreement may be fortuitous. This is not the case of our variatonal results and we have reported in the legend of Tab. VI, the ZPE of our calculations together with reference values. In fact, as also displayed in Tab. IV, where a convergence pattern is observed with basis set extension, our results are quite reliable. Note, also that cc-pVDZ with 8 sets of 2s basis sets is enough to obtain meaningful fundamental frequencies. Such a calculation takes only a few seconds of CPU time on a laptop (processor: Intel quadriCore i5 CPU M520 at 2.40 GHz, RAM: 6 Go), once the integrals have been computed. The integral computation bottleneck, which is not yet parallelized took about 4.5 min.

As we go towards heavier isotopologues in Tab. VI, our vibrational transition predictions improve whereas the electronic transition one deteriorates. This can be understood by the fact that the vibrational basis is limited to 16 functions. In the case of H_2, excited Kratzer functions multiplied by the lowest approximate electronic state can probably overlap with the lowest Kratzer functions multiplied by the approximate electronic excited state, and the differences in the sums of vibrational plus electronic energies should remain relatively small. So, a perturbation theory argument leads to the conclusion that these product functions can combine linearly and reconstitute properly both the global GS and the lowest electronic excited states. This is not the case of D_2 and T_2, where even the highest Kratzer function is much lower than the lowest electronic excited state. In contrast, the Kratzer functions multiplied by the approximate electronic GS will have closer total energies in D_2 and T_2 than in H_2, and will form a locally "dense" basis set to accurately describe the lowest vibrational levels of D_2 and T_2 isotopologues.

Note that performing usual (i.e. without reduced mass correction) BO calculations for H_2 with the same basis (that is to say: 16 sets of 2s basis sets located on both sides of cc-pV5Z H-atom basis with a step size of 0.08 au) at Full CI level for the grid of points (0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 3.0, 3.4, 3.8, 4.2) in au, then fitting the PES to a 7^{th}-order polynomial, and finally, solving the vibrational Schrödinger equation, we obtained the following energy differences from the vibrational GS: 4205.3cm^{-1} and 8158.6cm^{-1} . These numbers are higher than both EN-MFCI results with the same electronic basis set and the experimental values.

Turning now at the rotational energy differences for the electronic GS, we compared our results to the accurate values of Matyus and Reiher[40], and to the perturbative results of Pachucki and Komasa[85]. We did not quote those that include relativistic and/or QED corrections such as[89,90]. We see in Tab. VII that, the lowest rotational levels are predicted within 1 or 2 wave number accuracy for all vibrational levels. Not surprinsingly, the quality of our variational results deteriorates as energy increases, whether it is vibrational or rotational energy. However, very good values are obtained for the vibrational GS as high as $J = 14$.

V. CONCLUSION

The EN-GMFCI approach remedy to 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 other approaches for nuclear dof's.

Second, the EN-GMFCI method only couples the electronic and nuclear degrees of freedom after having obtained possibly already 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 product basis functions. However, the electronic mean field Hamiltonians can capture the dominant electronic correlations.

The energy expression for diatomic EN-MFCI 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. Numerical results on dihydrogen isotopologues reveal that our approach is able to compute vibrational and electronic levels within a few wave numbers in a single calculation. Duplicating such calculation for different J-values gives also rotational energy levels within the wave number accuracy.

However, the EN-MFCI method is still at an embryonic stage and as not yet been fully implemented. Many aspects remain to be developed and studied carefully. We review some of them below.

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

Dealing with polyatomics having more nuclear dofs will result in non separable integrals of large dimensionality. One will have to use numerical techniques as already developed for purely ro-vibrational calculations[82,97,98] or (quasi) Monte-Carlo techniques recently developed in mathematics[81] and therein.

Truncation of the product basis set should also be implemented and taken advantage of to tackle larger systems, or small systems such as those studied here, but with larger basis sets to reach convergence of the Hamiltonian eigenvalues to the μHartree accuracy. However, the next point should be adressed first.

Special basis set appropriately suited to perform EN-GMFCI need to be developed. For the nuclear dof's, one needs basis functions such that $\frac{1}{Q}$ integrals converge, such as Kratzer basis functions, suitable to describe all types of internal motion, not only bond stretching. For electronic dof's, one needs to modify standard Gaussian basis sets to describe an electronic cloud smeared by the vibrational motion of the nuclear centers. In particular for diatomics, nucleus-centered core orbitals, must be replaced by segment-centered orbitals and formulas for matrix elements must be adapted accordingly. For polyatomics, ellipsoid centered orbitals would be needed. Work is in progress along these lines of research.

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APPENDIX A: RYS / GENERALIZED LAGUERRE DOUBLE QUADRATURE FORMULAS FOR ELECTRON-NUCLEUS INTEGRALS

The most general electron-nucleus Coulomb integrals that will appear in our diatomic calculations are of the form:

$$I_{e-n}[Z_I, r^0_{I_z}, \eta] = \langle \phi^{kra}_i(Q)\chi_1(\vec{r^e})| \frac{Z_I}{\sqrt{(r^e_x)^2 + (r^e_y)^2 + (r^e_z - r^0_{I_z} + \eta Q)^2}} |\phi^{kra}_j(Q)\chi_2(\vec{r^e})\rangle, \tag{32}$$

where the χ_i's are primitive Gaussian functions of the form given in Eq. (21) and the ϕ^{kra}_i's are Kratzer basis functions:

$$\phi^{kra}_i(Q) = \frac{N^{kra}_i}{\sqrt{\xi^0_{ab}}} \left(1 + \frac{Q}{\xi^0_{ab}}\right)^{\lambda} Exp\left[\frac{\lambda(1-\lambda)}{\lambda + i}(1 + \frac{Q}{\xi^0_{ab}})\right] \,_1F_1[-i, 2\lambda; \frac{2\lambda(\lambda-1)}{\lambda+i}\left(1 + \frac{Q}{\xi^0_{ab}}\right)]. \tag{33}$$

The normalization factor N^{kra}_i is

$$N^{kra}_i = \frac{1}{\Gamma[2\lambda]} \left(\frac{2\lambda(\lambda-1)}{i+\lambda}\right)^{\lambda+\frac{1}{2}} \sqrt{\frac{\Gamma[2\lambda+i]}{2(i+\lambda)i!}}, \tag{34}$$

and the confluent hypergeometric function ${}_1F_1[a, c; x]$ (see Ref.[74]) appearing in Eq. (33), is in fact a polynomial of degree i. Setting $\tilde{r}^0_{I_z} = r^0_{I_z} + \eta\xi^0_{ab}$, $\tilde{\eta} = \eta\xi^0_{ab}$, $\alpha = \left(1 + \frac{Q}{\xi^0_{ab}}\right)$, and,

$$I_{e-n}[Z_I, r^0_{I_z}, \eta] = Z_I N_1 N_2 N_i^{kra} N_j^{kra} \tilde{I}_{e-n}[\tilde{r}^0_{I_z}, \tilde{\eta}] \tag{35}$$

we have to calculate,

$$\begin{aligned}\tilde{I}_{e-n}[\tilde{r}^0_{I_z}, \tilde{\eta}] &= \int_0^{+\infty} d\alpha\ \alpha^{2\lambda}\ {}_1F_1[-i, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+i}\alpha]\ {}_1F_1[-j, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+j}\alpha] Exp\left[\tfrac{\lambda(2\lambda+i+j)}{(\lambda+i)(\lambda+j)}(1-\lambda)\alpha\right] \\ &\times \int_{-\infty}^{+\infty} dr_x^e \int_{-\infty}^{+\infty} dr_y^e \int_{-\infty}^{+\infty} dr_z^e Exp\left[-(\zeta_1+\zeta_2)(r_x^e)^2\right] Exp\left[-(\zeta_1+\zeta_2)(r_y^e)^2\right] \\ &\times Exp\left[-\zeta_1(r_z^e - r^0_{1_z})^2 - \zeta_2(r_z^e - r^0_{2_z})^2\right] \frac{(r_x^e)^{l_1+l_2}(r_y^e)^{k_1+k_2}(r_z^e - r^0_{1_z})^{j_1}(r_z^e - r^0_{2_z})^{j_2}}{\sqrt{(r_x^e)^2 + (r_y^e)^2 + (r_z^e - \tilde{r}^0_{I_z} + \tilde{\eta}\alpha)^2}}\end{aligned} \tag{36}$$

The square root can be transformed using Laplace transform and assuming that the integrals commute, one can integrate over electronic variables:

$$\begin{aligned}\tilde{I}_{e-n}[\tilde{r}^0_{I_z}, \tilde{\eta}] &= \int_0^{+\infty} d\alpha\ \alpha^{2\lambda}\ {}_1F_1[-i, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+i}\alpha]\ {}_1F_1[-j, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+j}\alpha] Exp\left[\tfrac{\lambda(2\lambda+i+j)}{(\lambda+i)(\lambda+j)}(1-\lambda)\alpha\right] \\ &\int_0^{+\infty} \frac{d\beta}{\sqrt{\pi\beta}} \int_{-\infty}^{+\infty} dr_x^e (r_x^e)^{l_1+l_2} Exp\left[-(\zeta_1+\zeta_2+\beta)(r_x^e)^2\right] \int_{-\infty}^{+\infty} dr_y^e (r_y^e)^{k_1+k_2} Exp\left[-(\zeta_1+\zeta_2+\beta)(r_y^e)^2\right] \\ &\times \int_{-\infty}^{+\infty} dr_z^e (r_z^e - r^0_{1_z})^{j_1}(r_z^e - r^0_{2_z})^{j_2} Exp\left[-\zeta_1(r_z^e - r^0_{1_z})^2 - \zeta_2(r_z^e - r^0_{2_z})^2 - \beta(r_z^e - \tilde{r}^0_{I_z} + \tilde{\eta}\alpha)^2\right]\end{aligned}$$

$$\begin{aligned}&= \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}} \Gamma\left[\tfrac{k_1+k_2+1}{2}\right] \Gamma\left[\tfrac{l_1+l_2+1}{2}\right] Exp\left[-\tfrac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z} - r^0_{2_z})^2\right] \\ &\times \int_0^{+\infty} d\alpha\ \alpha^{2\lambda}\ {}_1F_1[-i, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+i}\alpha]\ {}_1F_1[-j, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+j}\alpha] Exp\left[\tfrac{\lambda(2\lambda+i+j)}{(\lambda+i)(\lambda+j)}(1-\lambda)\alpha\right] \\ &\times \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1+\zeta_2+\beta)^{-\frac{k_1+k_2+l_1+l_2}{2}-1} Exp\left[-\tfrac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\tfrac{\zeta_1 r^0_{1_z} + \zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2} - \tilde{r}^0_{I_z} + \tilde{\eta}\alpha\right)^2\right] \\ &\times \int_{-\infty}^{+\infty} dr_z^e (r_z^e - r^0_{1_z})^{j_1}(r_z^e - r^0_{2_z})^{j_2} Exp\left[-\left(\zeta_1+\zeta_2+\beta)(r_z^e - \tfrac{\zeta_1 r^0_{1_z} + \zeta_2 r^0_{2_z} + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha)}{\zeta_1+\zeta_2+\beta}\right)^2\right]\end{aligned}$$

$$\begin{aligned}&= \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}} \Gamma\left[\tfrac{k_1+k_2+1}{2}\right] \Gamma\left[\tfrac{l_1+l_2+1}{2}\right] Exp\left[-\tfrac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z} - r^0_{2_z})^2\right] \sum_{i_1=0}^{j_1}\sum_{i_2=0}^{j_2} \binom{j_1}{i_1}\binom{j_2}{i_2} \delta^{[2]}_{0,i_1+i_2} \Gamma\left[\tfrac{i_1+i_2+1}{2}\right] \\ &\times \int_0^{+\infty} d\alpha\ \alpha^{2\lambda}\ {}_1F_1[-i, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+i}\alpha]\ {}_1F_1[-j, 2\lambda; \tfrac{2\lambda(\lambda-1)}{\lambda+j}\alpha] Exp\left[\tfrac{\lambda(2\lambda+i+j)}{(\lambda+i)(\lambda+j)}(1-\lambda)\alpha\right] \\ &\times \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1+\zeta_2+\beta)^{-\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2}} \left(\zeta_2(r^0_{2_z} - r^0_{1_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{1_z})\right)^{j_1-i_1} \\ &\times \left(\zeta_1(r^0_{1_z} - r^0_{2_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{2_z})\right)^{j_2-i_2} Exp\left[-\tfrac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\tfrac{\zeta_1 r^0_{1_z} + \zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2} - \tilde{r}^0_{I_z} + \tilde{\eta}\alpha\right)^2\right],\end{aligned} \tag{37}$$

where $\delta^{[2]}_{0,k}$ is 0 or 1 according to k being odd or even, and, where for $i_1 = j_1$, (respectively, $i_2 = j_2$), the undetermined factor $\left(\zeta_2(r^0_{2_z} - r^0_{1_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{1_z})\right)^{j_1-i_1}$, (respectively, $\left(\zeta_1(r^0_{1_z} - r^0_{2_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{2_z})\right)^{j_2-i_2}$), should be set to 1, when $\zeta_2(r^0_{2_z} - r^0_{1_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{1_z}) = 0$, (respectively, $\zeta_1(r^0_{1_z} - r^0_{2_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{2_z}) = 0$).

Let us consider first the integral over β,

$$I_\beta[i_1, i_2, \alpha] = \int_0^{+\infty} d\beta\ \beta^{-\frac{1}{2}}(\zeta_1 + \zeta_2 + \beta)^{-\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2}} \left(\zeta_2(r^0_{2_z} - r^0_{1_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{1_z})\right)^{j_1-i_1}$$
$$\times \left(\zeta_1(r^0_{1_z} - r^0_{2_z}) + \beta(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{2_z})\right)^{j_2-i_2} Exp\left[-\frac{(\zeta_1+\zeta_2)\beta}{\zeta_1+\zeta_2+\beta}\left(\frac{\zeta_1 r^0_{1_z} + \zeta_2 r^0_{2_z}}{\zeta_1+\zeta_2} - \tilde{r}^0_{I_z} + \tilde{\eta}\alpha\right)^2\right]. \tag{38}$$

Making the change of variable $\beta \to \gamma = \frac{\beta}{\zeta_1+\zeta_2+\beta}$ and using the binomial expansion if $(r^0_{1_z} - r^0_{2_z})$ is non zero, we obtain,

$$I_\beta[i_1, i_2, \alpha] = \sum_{s_1=0}^{j_1-i_1}\sum_{s_2=0}^{j_2-i_2}\binom{j_1-i_1}{s_1}\binom{j_2-i_2}{s_2}\zeta_1^{j_2-i_2-s_2}(-\zeta_2)^{j_1-i_1-s_1}(\zeta_1+\zeta_2)^{s_1+s_2-\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-1}$$
$$\times (r^0_{1_z} - r^0_{2_z})^{j_1+j_2-i_1-i_2-s_1-s_2}(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{1_z})^{s_1}(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{2_z})^{s_2} I_\gamma[s_1, s_2, \alpha]. \tag{39}$$

If $(r^0_{1_z} - r^0_{2_z}) = 0$, that is if the electronic orbitals are on the same center, the expression is simply,

$$I_\beta[i_1, i_2, \alpha] = (\zeta_1 + \zeta_2)^{-\frac{k_1+k_2+l_1+l_2+i_1+i_2+2}{2}}(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{1_z})^{j_1-i_1}(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha - r^0_{2_z})^{j_2-i_2} I_\gamma[j_1 - i_1, j_2 - i_2, \alpha]. \tag{40}$$

In the last two equations, $I_\gamma[s_1, s_2, \alpha]$ is defined to be,

$$I_\gamma[s_1, s_2, \alpha] = \int_0^{+1} d\gamma\ \gamma^{s_1+s_2-\frac{1}{2}}(1-\gamma)^{+\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-s_1-s_2}$$
$$\times Exp\left[-\frac{\left(\zeta_1 r^0_{1_z} + \zeta_2 r^0_{2_z} - (\zeta_1+\zeta_2)(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\ \gamma\right], \tag{41}$$

where we recognize the confluent hypergeometric function ${}_1F_1[a, c; x]$[74],

$$I_\gamma[s_1, s_2, \alpha] = \frac{\Gamma[s_1+s_2+\frac{1}{2}]\Gamma[\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2} - s_1 - s_2 + 1]}{\Gamma[\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2}]}$$
$$\times\ {}_1F_1\left[s_1 + s_2 + \frac{1}{2}, \frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2+3}{2}; -\frac{\left(\zeta_1 r^0_{1_z} + \zeta_2 r^0_{2_z} - (\zeta_1+\zeta_2)(\tilde{r}^0_{I_z} - \tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\right]. \tag{42}$$

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

$$I_\gamma[s_1,s_2,\alpha] = 2\int_0^{+1} d\tau\ \tau^{2(s_1+s_2)}(1-\tau^2)^{\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-s_1-s_2} \\ \times Exp\left[-\frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}\ \tau^2\right]. \tag{43}$$

the $\delta^{[2]}$ functions in Eq.(36) insure that the Rys quadrature will be exact, since $\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}$ 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,

$$n^{\rm Rys}_{\rm roots} = \frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}. \tag{44}$$

So, setting,

$$\nu(\alpha) = \frac{\left(\zeta_1 r^0_{1_z}+\zeta_2 r^0_{2_z}-(\zeta_1+\zeta_2)(\tilde{r}^0_{I_z}-\tilde{\eta}\alpha)\right)^2}{\zeta_1+\zeta_2}, \tag{45}$$

we can rewrite exactly $I_\gamma[s_1,s_2,\alpha]$ as a discretized Rys sum,

$$I_\gamma[s_1,s_2,\alpha] = 2\sum_p w^{\rm Rys}_p[\nu(\alpha)]\tau_p[\nu(\alpha)]^{2(s_1+s_2)}(1-\tau_p[\nu(\alpha)]^2)^{\frac{k_1+k_2+l_1+l_2+2j_1+2j_2-i_1-i_2}{2}-s_1-s_2}, \tag{46}$$

where the $\tau_p[\nu(\alpha)]$'s are the roots of the Rys polynomials, and $w^{\rm Rys}_p[\nu(\alpha)]$'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 generalized Laguerre-Gauss quadrature seems the most appropriate scheme[75]:

$$\tilde{I}_{e-n}[\tilde{r}^0_{I_z},\tilde{\eta}] = \frac{\delta^{[2]}_{0,k_1+k_2}\delta^{[2]}_{0,l_1+l_2}}{\sqrt{\pi}}\Gamma\left[\frac{k_1+k_2+1}{2}\right]\Gamma\left[\frac{l_1+l_2+1}{2}\right] Exp\left[-\frac{\zeta_1\zeta_2}{\zeta_1+\zeta_2}(r^0_{1_z}-r^0_{2_z})^2\right]\sum_{i_1=0}^{j_1}\sum_{i_2=0}^{j_2}\binom{j_1}{i_1}\binom{j_2}{i_2} \\ \times \delta^{[2]}_{0,i_1+i_2}\Gamma\left[\frac{i_1+i_2+1}{2}\right]\sum_q w^{\rm Lag}_q\ {}_1F_1[-i,2\lambda;\tfrac{2\lambda(\lambda-1)}{\lambda+i}\kappa_q]\ {}_1F_1[-j,2\lambda;\tfrac{2\lambda(\lambda-1)}{\lambda+j}\kappa_q]I_\beta[i_1,i_2,\kappa_q], \tag{47}$$

where κ_q and $w^{\rm Lag}_q$ are respectively the generalized Gauss-Laguerre polynomials roots and weights corresponding to parameters $\left(2\lambda+i+j,\frac{\lambda(2\lambda+i+j)}{(\lambda+i)(\lambda+j)}(\lambda-1)\right)$: that is to say, the appropriate roots and weights to integrate by quadrature an integral of the form,

$$\int_0^{+\infty} dx\ x^{2\lambda+i+j}Exp[-\frac{\lambda(2\lambda+i+j)}{(\lambda+i)(\lambda+j)}(\lambda-1)x]f(x). \tag{48}$$

Inserting Eq.(47) into Eq.(35) gives the required electron-nucleus attraction integrals.

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TABLES

Kratzer potential parameters (in au)

	$\mathbf{H_2}$	$\mathbf{D_2}$	$\mathbf{T_2}$
λ	36.754020	51.755767	63.224041
ξ^0_{ab}	42.430690	59.991167	73.415113

TABLE I. Kratzer potential parameters used for the vibrational modal basis sets of dihydrogen and isotopologues.

Convergence of H_2 ground state energy with number of modals and number of ghost atoms

	k=4	k=8	k=12	k=16
$n = 4$	-1.1621504	-1.1622377	-1.1622418	-1.1622419
$n = 8$	-1.1623184	-1.1624301	-1.1624334	-1.1624341
$n = 12$	-1.1623574	-1.1624676	-1.1624750	-1.1624754
$n = 16$	-1.1623887	-1.1624996	-1.1625050	-1.1625060

TABLE II. Convergence of H_2 ground state energy (hartree) with number of Kratzer basis functions, k, and the number of off-centered ghost atoms, n. The Kratzer basis functions used for the nuclear modal basis set are the lowest eigenfunctions of a Kratzer potential with parameters $\xi^0_{ab} = 42.430690$ au, $D = 0.364955174$ au. H-atom Dunning correlation basis sets CC-PVTZ[84] were locate at ± 0.70018162 au on the x-axis and ghost atom two s-orbital basis sets corresponding to the core $1s$-orbital of the cc-pVTZ H-basis plus the third uncontracted s-Gaussian primitive corresponding to exponent $1.159au$, were located on each side of each H-atom with a step size of ± 0.08 au . For example the first set of 4 ghost atoms were located at respectively ± 0.78018162 au and ± 0.62018162 au. A tolerance of 10^{-6} was used to eliminate quasi-linear dependencies of the electronic orbital basis set. Reduced mass correction is included.

Convergence of H_2 ground state energy with electronic basis

basis set: + n off-centered 2s	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
$n = 4$	-1.1576745 (18-0)	-1.1622419 (36-0)	-1.1632984 (68-0)	-1.1636441 (118-0)
$n = 8$	-1.1579290 (26-5)	-1.1624380 (44-4)	-1.1634754 (76-2)	-1.1638262 (126-0)
$n = 12$	-1.1581072 (34-10)	-1.1624953 (52-9)	-1.1635184 (84-5)	-1.1638365 (134-5)
$n = 16$	-1.1581475 (42-16)	-1.1625060* (60-16)	-1.1635140 (92-10)	-1.1638438 (142-8)

TABLE III. Convergence of H_2 ground state energy (hartree) with electronic orbital basis set. The 16 lowest eigenfunctions of a Kratzer potential with parameters $\xi^0_{ab} = 42.430690$ au, $D = 0.364955174$ au were used for the nuclear modal basis set. H-atom Dunning correlation basis sets[84] were locate at ± 0.70018162 au on the x-axis and two s-orbital basis sets corresponding to the contracted 1s-orbital of the cc-pVnZ H-basis plus the most diffuse primitive Gaussian not used as an uncontracted s-orbital in the H-basis, were located on each side of each atom with a step size of ± 0.08 au. A tolerance of 10^{-7} was used to eliminate quasi-linear dependencies of the electronic orbital basis set. In parenthesis, the first integer is the total number of orbital basis functions, the second integer is the number or quasi-linearly dependent functions removed. Reduced mass correction is included. These numbers should be compared with the value of Bubin et al.[86], -1.1640250308 Hartrees. However, note that our numbers do not include the non diagonal mass polarization contribution.

* Tolerance of 10^{-6} was used for this calculation.

Convergence of H_2 fundamental frequency with electronic basis

basis set: + n off-centered 2s	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
$n = 4$	4243.9614	4368.4358	4370.9965	4343.8847
$n = 8$	4167.3741	4221.7984	4223.5432	4213.2700
$n = 12$	4157.3350	4179.1580	4173.7389	4172.7935
$n = 16$	4151.8120	4172.7132*	4165.2741	4165.3588

TABLE IV. Convergence of H_2 fundamental frequency (cm^{-1}) with electronic orbital basis set. Details as in Tab. III. These numbers should be compared with the value of Bubin et al.[86], 4161.1641150762 cm^{-1} . However, note that our numbers do not include the non diagonal mass polarization contribution.

Convergence of H_2 ground state energy with MFCI iterations

iteration number	HF	Full CI
0	-1.1100467	-1.1508083
1	-1.1138025	-1.1546101
2	-1.1139342	-1.1547108
3	-1.1139687	-1.1547212
4	-1.1139925	-1.1547273
5	-1.1140094	-1.1547317
6	-1.1140215	-1.1547349
7	-1.1140300	-1.1547374
8	-1.1140360	-1.1547391
9	-1.1140404	-1.1547403
CV	-1.1140507	-1.1547436

TABLE V. Convergence of H_2 ground state energy (hartree) with MFCI iterations for different electronic methods: Hartree-Fock (HF) and Full configuration interactions (Full CI). The [cc-pV5Z + 16 (2s)]$\otimes$[16 Kratzer] basis corresponding to the last entries of Tabs. III and IV has been used. The vibrational method is always the Full CI. CV stands for "converged".

Vibrational and electronic transition wave numbers (in cm^{-1}) of H_2, D_2, and T_2.

	H_2				**D_2**				**T_2**			
Transition	TF-NOMO/CIS	TF-NOMO/FCI	this work	Exp.	TF-NOMO/CIS	TF-NOMO/FCI	this work	Exp.	TF-NOMO/CIS	TF-NOMO/FCI	this work	Exp.
$\nu :\ 0 \rightarrow 1$	4655	4182	4165	4161	3549	3006	2994	2994	2929	2477	2465	2465
$\nu :\ 0 \rightarrow 2$	9406	N/A	8110	8087	7026	N/A	5874	5869	5843	N/A	4851	4849
$\Sigma_g^+ :\ 0 \rightarrow 1$	106556	N/A	91711	91700	107628	N/A	92182	91697	108043	N/A	92375	91696

TABLE VI. Selected electronic and vibrational transitions of dihydrogen isotopologues (in cm^{-1}). "this work" corresponds to the [cc-pV5Z + 16 (2s)]$\otimes$[16 Kratzer] basis set and EN-MFCI calculation contracting electron and nuclei after a single MFCI iteration (see last entries of Tabs. III and IV). However, for D_2 and T_2 a step size of 0.07 ua instead of 0.08 ua has been chosen to spread off-centered orbitals because of the smaller vibrational motion amplitude. GS energy is -1.1669493 Hartree for D_2 (-1.1683018 resp. for T_2) to be compared with the non relativistic value, 1.16716880921 Hartree of Bubin et al.[87] (resp. -1.16853567568). Translation-Free NOMO (TF-NOMO) results and experimental (Exp.) numbers are taken from Nakai[26]. More precisely, the TF-NOMO/CIS results correspond to a cc-pVTZ electronic basis set and a (3s3p3d) nuclear basis set; the TF-NOMO/FCI results correspond to a (6s3p1d) electronic basis set and a (3s3p) nuclear basis set[99].

Selected rotational energy levels (in cm^{-1}) of H_2.

	this work	Ref.[85]	Ref.[40]
$\underline{\nu = \mathbf{0}}$			
$J = 1$	118.4	118.4851	118.485355
$J = 2$	354.1	354.3684	354.369007
$J = 3$	705.1	705.5097	705.509982
$J = 4$	1168.1	1168.7825	1168.782740
$J = 5$	1739.1	1740.1675	N/A
$J = 14$	10797.7	10800.9043	N/A
$\underline{\nu = \mathbf{1}}$			
$J = 1$	112.5	112.5730	N/A
$J = 2$	336.5	336.6682	N/A
$J = 3$	669.9	670.2172	N/A
$J = 4$	1109.7	1110.2000	N/A
$J = 5$	1652.2	1652.7361	N/A
$J = 14$	10257.8	10237.9613	N/A
$\underline{\nu = \mathbf{2}}$			
$J = 1$	107.0	106.7905	N/A
$J = 2$	319.9	319.3545	N/A
$J = 3$	637.0	635.6922	N/A
$J = 4$	1055.6	1052.8833	N/A
$J = 5$	1572.0	1567.1775	N/A
$J = 14$	9795.1	9684.4911	N/A
$\underline{\nu = \mathbf{5}}$			
$J = 1$	88.3	89.7800	N/A
$J = 2$	264.5	268.4120	N/A
$J = 3$	527.8	534.0707	N/A
$J = 4$	876.7	884.0925	N/A
$J = 5$	1309.0	1168.7825	N/A
$J = 14$	8218.6	8029.4047	N/A

TABLE VII. First rotational energy levels of dihydrogen (in cm^{-1}). "this work" corresponds to the [cc-pV5Z + 16 (2s)]$\otimes$[16 Kratzer] basis set and EN-MFCI calculation contracting electron and nuclei after a single MFCI iteration.