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► **To cite this version:**

Patrick Cassam-Chenaï, Bingbing Suo, Wenjian Liu. A Quantum Chemical Definition of Electron-Nucleus Correlation. *Theoretical Chemistry Accounts: Theory, Computation, and Modeling*, 2017, 10.1007/s00214-017-2081-3 . hal-01184301v3

HAL Id: hal-01184301

<https://hal.science/hal-01184301v3>

Submitted on 22 Sep 2016

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A Quantum Chemical Definition of Electron-Nucleus Correlation

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(Dated: 22 September 2016)

We introduce a definition of electron-nucleus correlation energy by analogy with the quantum chemical definition of electronic correlation energy. The uncorrelated reference function is obtained by repeated electron-nucleus mean field configuration interaction steps until self-consistency is achieved. Electron-nucleus correlation and electronic correlation energies are compared on dihydrogen isotopologues.

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I. INTRODUCTION

The importance of electron-nucleus correlation in molecular systems has triggered the introduction of explicitly correlated basis functions¹⁻¹⁴ in non-Born-Oppenheimer methods. However, the attempts to quantify electron-nucleus correlation energy in molecular systems are rather scarce, with a few notable exceptions¹⁵⁻²¹.

In this article, we define the electron-nucleus correlation energy by analogy with the quantum chemical definition of the electronic correlation energy, as the difference between the exact energy of a molecular state and its best approximate as a direct product wave function. Both electron and nucleus wave functions are general wave functions of full configuration interaction (CI) type, that is to say, they include electronic correlation and nuclear motion correlation respectively. However, in contrast to the Born-Oppenheimer or adiabatic approaches, the electronic wave function does not depend parametrically upon nuclear variables, so that there is no built-in electron-nucleus correlation already accounted for in the direct product ansatz.

We show on the dihydrogen isotopologues example, that electron-nucleus correlation is quantitatively less important than electronic correlation, the heavier the isotopologue the larger the difference. In fact, electron-nucleus correlation is found roughly proportional to the vibrational energy of the molecular state. Our interpretation is that the heavier the isotopologue, the less its vibrational energy and vibrational amplitude, the closer to the clamped nuclei limit, the better the direct product approximation.

The article is organized as follows: We first define formally electron-nucleus correlation explaining the rationale behind it. Then, we briefly recall the theory of the electron-nucleus mean field configuration interaction (EN-MFCI) method²², which allows one to compute this quantity, since it encompasses as particular cases the best electron-nucleus direct product wave function ansatz and the exact full CI electron-nucleus ansatz for a given finite basis set. Finally, the calculated electron-nucleus and electronic correlation energies are compared quantitatively for dihydrogen isotopologues. In addition, two appendices give complements on the relationship between electron-nucleus coupling and electron-nucleus correlation, and on the clamped nuclei limit.

II. ELECTRON-NUCLEUS CORRELATION ENERGY

In probability theory, two events “ A ” and “ B ” are said independent, that is to say, “uncorrelated”, if and only if the probability of observing A and B is the product of the probability of observing A by the probability of observing B : $p(A \wedge B) = p(A) \cdot p(B)$. According to the Born interpretation of quantum mechanics, the square of the normalized wave function of a quantum system, $|\psi(r)|^2 := p(r)$ is the probability of observing the system at configuration point r . Putting these two elements together, we see that a Hartree product wave function for a bipartite quantum system, $\psi_H(r_1, r_2) = \psi_1(r_1)\psi_2(r_2)$ is uncorrelated in the probabilistic sense, since $|\psi_H(r_1, r_2)|^2 = |\psi_1(r_1)|^2 |\psi_2(r_2)|^2$.

The situation is somewhat less simple for a Fermionic system such as the electrons of a molecular system. A Slater determinant type of wave function, $\psi_S(r_1, r_2) = \frac{\psi_1(r_1)\psi_2(r_2) - \psi_1(r_2)\psi_2(r_1)}{\sqrt{2}}$, which is the fermionic equivalent of a Hartree product of distinguishable particles, has already some built-in correlation, as in general, one has $|\psi_S(r_1, r_2)|^2 \neq |\psi_1(r_1)|^2 |\psi_2(r_2)|^2$. However, this correlation in the probabilistic sense is just Pauli spin statistic correlation, as can be inferred from the wedge product notation $\psi_1 \wedge \psi_2$ of the same Slater determinantal wave function, where antisymmetry is built-in. So, in the Fermionic case, the “uncorrelated” reference is still chosen to be the Slater determinant ansatz, and in quantum chemistry the electronic correlation energy is defined as the difference between the electronic full configuration interaction (E-FCI) energy and the lowest energy achievable with a Slater determinantal function that is to say, with an Hartree-Fock (HF) wave function (disregarding symmetry considerations):

$$E_{correl}^{el} = \langle \psi_{E-FCI} | H | \psi_{E-FCI} \rangle - \langle \psi_{HF} | H | \psi_{HF} \rangle. \quad (1)$$

Considering now a molecular system composed of a set of electrons, with position and spin variables collectively denoted by \vec{R}^e and a set of nuclei, with position and spin variables collectively denoted by \vec{R}^n , the uncorrelated reference ansatz will be the Hartree product,

$$\psi_H(\vec{R}^n, \vec{R}^e) = \psi_n(\vec{R}^n)\psi_e(\vec{R}^e), \quad (2)$$

since both sets, electrons and nuclei are clearly distinguishable. Note that such a product can be regarded mathematically as a tensor product, $\psi_H = \psi_n \otimes \psi_e$. Then, it is natural

to define the electron-nucleus correlation energy, by analogy with Eq.(1), as

$$E_{correl}^{EN} = \langle \psi_{EN-FCI} | H | \psi_{EN-FCI} \rangle - \frac{Min}{\psi_H} \langle \psi_H | H | \psi_H \rangle, \quad (3)$$

that is to say, as the difference between the electron-nuclear full configuration interaction (EN-FCI) energy and the lowest energy achievable with a Hartree product of the form given by Eq.(2). Let us emphasize that both the electronic, ψ_e , and nuclear, ψ_n , wave functions are completely general functions of the electronic and nuclear Hilbert spaces, respectively. That is to say, they are what would be called FCI-type wave functions in a finite basis set context: ψ_e fully accounts for the correlation of the electrons in the mean field of ψ_n . Conversely, ψ_n fully accounts for nuclear motion correlation in the mean field of ψ_e . The fact that our reference “uncorrelated” EN-wave function is the direct product of two FCI-type wave functions, is not in contradiction with our claim of generalizing the electronic correlation definition. Indeed, HF-optimized orbitals can also be regarded as “FCI” solutions of a one-particle mean-field problem at every step of the self-consistent field (SCF) process.

The fundamental difference with respect to the Born-Oppenheimer (BO) ansatz²³, or to the general coordinate approach (see Ref.²⁴ and therein), is that the electronic wave function ψ_e in ψ_H does not depend parametrically upon the nuclear coordinates. Algebraically, the “electronic” factor of a Born-Oppenheimer type wave function $\psi_{BO}(\vec{R}^n, \vec{R}^e) = \psi_n(\vec{R}^n)\psi_e(\vec{R}^n, \vec{R}^e)$ can always be decomposed as $\psi_e(\vec{R}^n, \vec{R}^e) = \sum_i \psi_1^i(\vec{R}^n) \otimes \psi_2^i(\vec{R}^e)$, and the “nuclear” factor acts multiplicatively as an operator on the first component: $\psi_n(\vec{R}^n)[\psi_e(\vec{R}^n, \vec{R}^e)] = \sum_i (\psi_n(\vec{R}^n)\psi_1^i(\vec{R}^n)) \otimes \psi_2^i(\vec{R}^e)$. The difference with the Hartree product is clear: the expansion is not limited to a single term. So, there will be, in general, some built-in electron-nucleus correlation. As a matter of fact, we know²⁵ that in general, $|\psi_e(\vec{R}^n, \vec{R}^e)|^2 \neq |\psi_1(\vec{R}^n)|^2 |\psi_2(\vec{R}^e)|^2$. Moreover, minimising the energy of such a BO-type wave function would give nothing else but the EN-FCI result, $E_{EN-FCI} = \frac{Min}{\psi_{BO}} \langle \psi_{BO} | H | \psi_{BO} \rangle$, since the EN-FCI wave function can always be expressed in this form^{26,27}.

Our reference wave function is clearly different from the NOMO-HF (nuclear orbital molecular orbital Hartree-Fock) aka NEO-HF ((nuclear-electronic orbital Hartree-

Fock) aka MCMO-HF (multicomponent molecular orbital Hartree-Fock) aka APMO-HF ((Any-Particle Molecular orbital Hartree-Fock) reference wave function used in previous electron-nucleus correlation energies calculations¹⁵⁻²¹, (unless the system consists of only a single electron and a single nucleus), because it fully includes the electron-electron and nucleus-nucleus correlations. However, the electron-nucleus correlation energies calculated within the MP2-perturbative framework, are independent from electron-electron or nucleus-nucleus correlations²⁸, so should be comparable with ours. The order of magnitude found in^{18,21} is compatible with that obtained from our definition in Section IV. In contrast, the order of magnitude of electron-nucleus correlation energies reported in¹⁵ are about three times larger. In fact, this discrepancy was due to contamination by translations and rotations, as can be seen from Table III of Ref.¹⁹ or Tab.III of Ref.²⁰.

Let us mention that, in the same way as the HF wave function can be a bad reference wave function for some electronic systems (typically, systems exhibiting strong “static” correlation), the best Hartree-product wave function can be inappropriate to describe correctly some situations, for example when two electronic states are degenerate at a conical intersection of BO surfaces, or in a double well situation¹⁶.

As we shall see in the next section, the wave function achieving the lowest Hartree product energy, is the solution of the EN-MFCI method²² iterated until self-consistency is achieved, when FCI is used to solve both the electronic and nuclear motion effective Hamiltonians.

III. THE ELECTRON-NUCLEUS MEAN FIELD CONFIGURATION INTERACTION (EN-MFCI) METHOD

Let us consider a molecular system made of p electrons and N nuclei of masses (m_1, \dots, m_N) and charges (Z_1, \dots, Z_N) . The total nuclear mass will be denoted by M_N : $M_N = \sum_{a=1}^N m_a$. Let $(\vec{r}_1^e, \vec{r}_2^e, \dots, \vec{r}_p^e)$ denote the electronic position variables and $(\vec{r}_1^n, \vec{r}_2^n, \dots, \vec{r}_N^n)$ the nuclear position variables. Let us choose the center of nuclear mass as origin, to separate off the center-of-mass motion. This choice is convenient because the nuclear and electronic kinetic energy operators remain uncoupled²⁹ in this frame, how-

ever the EN-MFCI method could be presented in a more general setting. So, the nuclear position are transformed by a non singular, linear mapping \hat{L} to $(3N-3)$ translationally-invariant internal-Cartesian coordinates, $(Q_1, Q_2, \dots, Q_{3N-3}) := \vec{Q}^t$ (vectors are assumed to be column vectors and their transposed line vectors), plus the coordinates of their center of mass \vec{r}_{CNM}^n :

$$\begin{pmatrix} \vec{Q} \\ \vec{r}_{CNM}^n \end{pmatrix} = \hat{L} \begin{pmatrix} \vec{r}_1^n \\ \dots \\ \vec{r}_N^n \end{pmatrix} \quad (4)$$

with, $\forall i \in \{1, \dots, 3N-3\}, \forall k \in \{0, 1, 2\}, \sum_{a=1}^N L_{i,3a-k} = 0$, and $\forall k, l \in \{0, 1, 2\}, \forall a \in \{1, \dots, N\}$, if $k \neq l$ then $L_{3N-k,3a-l} = 0$ else $L_{3N-k,3a-k} = \frac{m_a}{M_N}$.

The above formula can be inverted so that

$$\vec{r}_a^n = \hat{L}_a^{-1} \begin{pmatrix} \vec{Q} \\ \vec{r}_{CNM}^n \end{pmatrix}, \quad (5)$$

\hat{L}_a^{-1} being the $(3 \times 3N)$ submatrix of \hat{L}^{-1} corresponding to nucleus a . For the case, assumed here, of a center of nuclear mass kept fixed at the origin, we may write somewhat abusively, $\vec{r}_a^n = \hat{L}_a^{-1} \vec{Q}$, (that is to say, we use the same notation for the operators \hat{L}_a^{-1} and for their restriction to the space of translation-free coordinates).

The molecular translation-free Coulomb Hamiltonian (in atomic units) can be decomposed into three parts: A purely electronic Hamiltonian

$$\hat{H}(\vec{R}^e) = -\frac{1}{2\mu_e} \sum_{i=1}^p \Delta_{\vec{r}_i^e} + \sum_{1 \leq i < j \leq p} \frac{1}{\|\vec{r}_i^e - \vec{r}_j^e\|} - \frac{\nabla_{\vec{r}_i^e}^t \cdot \nabla_{\vec{r}_j^e}}{M_N}, \quad (6)$$

where $\mu_e = \frac{M_N}{1+M_N}$ is the reduced mass of the electron, and $\frac{-1}{M_N} \sum_{1 \leq i < j \leq p} \nabla_{\vec{r}_i^e}^t \cdot \nabla_{\vec{r}_j^e}$ the so-called ‘‘non-diagonal mass polarization’’ term; a purely nuclear Hamiltonian,

$$\hat{H}(\vec{Q}) = -\frac{1}{2} \sum_{k,l=1}^{3N-3} \frac{1}{\mu_{k,l}} \frac{\partial^2}{\partial Q_k \partial Q_l} + \sum_{1 \leq a < b \leq N} \frac{Z_a Z_b}{\|\hat{L}_a^{-1} \vec{Q} - \hat{L}_b^{-1} \vec{Q}\|}, \quad (7)$$

where, $\frac{1}{\mu_{k,l}} = \sum_{a=1}^N \sum_{j=0}^2 \frac{L_{k,3a-j} L_{l,3a-j}}{m_a}$ and an electron-nucleus interaction term,

$$\hat{H}(\vec{R}^e, \vec{Q}) = -\sum_{i=1}^p \sum_{a=1}^N \frac{Z_a}{\|\vec{r}_i^e - \vec{r}_a^0 - \hat{L}_a^{-1} \vec{Q}\|}. \quad (8)$$

An EN-MFCI iteration step consists in solving the eigenvalue problem for either an electronic mean field Hamiltonian of the form,

$$\hat{H}^{eff}(\vec{R}^e) = \hat{H}(\vec{R}^e) + \langle \phi(\vec{Q}) | \hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e, \vec{Q}) | \phi(\vec{Q}) \rangle_{\vec{Q}} \quad (9)$$

where $\langle | \rangle_{\vec{Q}}$ means that integration is carried out only for nuclear coordinates, (so, the first term in the bracket on the right-hand side is just a constant: $\langle \phi(\vec{Q}) | \hat{H}(\vec{Q}) | \phi(\vec{Q}) \rangle_{\vec{Q}}$), or for a nuclear motion mean field Hamiltonian of the form,

$$\hat{H}^{eff}(\vec{Q}) = \hat{H}(\vec{Q}) + \langle \phi(\vec{R}^e) | \hat{H}(\vec{R}^e) + \hat{H}(\vec{R}^e, \vec{Q}) | \phi(\vec{R}^e) \rangle_{\vec{R}^e} \quad (10)$$

where $\langle | \rangle_{\vec{R}^e}$ means that integration is carried out for electronic coordinates only (so, the first term in the bracket on the right-hand side is just a constant: $\langle \phi(\vec{R}^e) | \hat{H}(\vec{R}^e) | \phi(\vec{R}^e) \rangle_{\vec{R}^e}$).

The electron-nucleus self-consistent field configuration interaction (EN-SCFCI) method consists in performing alternatively EN-MFCI iterations for electronic and nuclear motion degrees-of-freedom (dof's) using the ground state solution of the previous step, $\phi_0^{(n-1)}$, to build the mean field correction of the current iteration. The solution of step n provides a new approximate ground state $\phi_0^{(n)}$ which in turn can be used for step $n + 1$, and so on ... For example, if one starts at step 0 by solving an electronic problem with a given approximate nuclear motion wave function $\phi_0^{(0)}(\vec{Q})$, at even iteration numbers the electronic Hamiltonian will be:

$$\hat{H}^{eff(2l)}(\vec{R}^e) = \hat{H}(\vec{R}^e) + \langle \phi_0^{(2l)}(\vec{Q}) | \hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e, \vec{Q}) | \phi_0^{(2l)}(\vec{Q}) \rangle_{\vec{Q}} \quad (11)$$

and at odd iteration numbers the nuclear Hamiltonian will be

$$\hat{H}^{eff(2l+1)}(\vec{Q}) = \hat{H}(\vec{Q}) + \langle \phi_0^{(2l+1)}(\vec{R}^e) | \hat{H}(\vec{R}^e) + \hat{H}(\vec{R}^e, \vec{Q}) | \phi_0^{(2l+1)}(\vec{R}^e) \rangle_{\vec{R}^e}. \quad (12)$$

Setting $H_{tot} = \hat{H}(\vec{Q}) + \hat{H}(\vec{R}^e) + \hat{H}(\vec{R}^e, \vec{Q})$, we have:

$$\langle \phi_0^{(2l)} \phi_0^{(2l+1)} | H_{tot} | \phi_0^{(2l)} \phi_0^{(2l+1)} \rangle = \langle \phi_0^{(2l+1)} | \hat{H}^{eff(2l)} | \phi_0^{(2l+1)} \rangle_{\vec{R}^e} \quad (13)$$

So, if $\hat{H}^{eff(2l)} \psi = E \psi$ is solved variationally and if the variational space includes $\phi_0^{(2l-1)}$, then the variational principle implies that,

$$\langle \phi_0^{(2l+1)} | \hat{H}^{eff(2l)} | \phi_0^{(2l+1)} \rangle_{\vec{R}^e} \leq \langle \phi_0^{(2l-1)} | \hat{H}^{eff(2l)} | \phi_0^{(2l-1)} \rangle_{\vec{R}^e}, \quad (14)$$

hence

$$\dots \leq \langle \phi_0^{(2l)} \phi_0^{(2l+1)} | H_{tot} | \phi_0^{(2l)} \phi_0^{(2l+1)} \rangle \leq \langle \phi_0^{(2l-1)} \phi_0^{(2l)} | H_{tot} | \phi_0^{(2l-1)} \phi_0^{(2l)} \rangle \leq \dots \quad (15)$$

Therefore, for a total Hamiltonian bounded from below, such as the Coulomb translation-free Hamiltonian³⁰, the process ought to converge. Unless it gets stuck in another possible stationary solution, we may expect it to converge to the wave function achieving the lowest possible total energy of the variational space: $V = V_{FCI}^{nucl} \otimes V_{FCI}^{elec}$. That is to say, to best wave function of the Hartree-product form given in Eq.(2) whose energy expectation value is required to compute the correlation energy of Eq.(3).

When finite electronic and nuclear basis sets are used, after an arbitrary number, say n , of EN-MFCI iterations (from n equal zero to the number of iterations achieving SCF convergence within a chosen tolerance threshold), it is possible within the EN-MFCI framework to contract the electronic and nuclear dof's, that is to say, to perform an electron-nucleus configuration interaction (EN-CI) calculation. If all product functions $\{\phi_i^{2l} \phi_j^{2k+1}\}_{(i,j)}$ are constructed from the eigensolutions of any arbitrary steps (but of different parity, of course), say $\{\phi_i^{2l}\}_i$, and $\{\phi_j^{2k+1}\}_j$, and used for an EN-CI calculation, then one will obtain the EN-FCI solution, whose expectation value, $E_{EN-FCI} = \langle \psi_{EN-FCI} | H | \psi_{EN-FCI} \rangle$, is also required to compute Eq.(3).

IV. CORRELATION ENERGY: COMPARISON ON DIHYDROGEN ISOTOPOLOGUES

In the case of diatomic molecules, the rotational motion of the molecule as a whole can be exactly factored out of the nuclear Hamiltonian. Here, we only consider $J = 0$ i.e. totally symmetrical states with respect to rotational invariance and singlet electronic states. So, the nuclear motion problem is reduced to a one-dimensional, vibrational equation, and there is no nuclear motion correlation.

As case-examples, we consider the dihydrogen isotopologues, for which EN-FCI can be carried out. Basis functions have to be chosen carefully for both nuclear and electronic dof's. For the vibrational dof, we use Kratzer potential eigenfunctions^{31,32} with quantum

number less than a given parameter $N_{kra} - 1$, as in our previous study²². This choice is suitable for a bond stretching vibration and gives non divergent Coulomb integrals. For the electronic basis set, care must be taken that the usual orbital basis sets found in all quantum chemistry packages are designed for BO-type calculations, and are not suitable to represent smeared electron densities, see Fig.1. In fact, no matter how large a selected cc-pVnZ basis set, for example, is (i.e. no matter how large n is within available values), the fundamental vibrational frequency for H₂ comes out a factor 2 or more too large. This problem is fixed by spreading core electron orbitals along the vibrational axis on both sides of the nuclei. It is not necessary to spread valence electron orbitals which have a radii wider than the vibrational displacements. The fact that valence electrons are much less correlated to nuclear motion than core electrons was reported in¹⁵.

More precisely, the same Kratzer potential as in our previous work²² (equilibrium distance $r_e = 1.40036324$ a.u. and dissociation constant $D_e = .364955$ hartrees) is used. The vibrational basis set for a given isotopologue is constituted by the 16 lowest eigenfunctions of the model Hamiltonian made of this potential and a kinetic term with the reduced mass of the isotopologue considered. Regarding the electronic orbital basis sets, two cc-pV5Z of H-atom orbital basis sets³³ are located apart from each other at the distance $r_e = 1.40036324$ a.u. used for the Kratzer potential. Additional off-centered orbital sets made of two 1s orbitals: the contracted 1s-orbital of the cc-pV5Z H-basis plus an uncontracted s -orbital with exponent 0.0448780, are spread along the nuclear axis. For homonuclear isotopologues, the same positions as in our previous study are used for the off-centered orbital sets, that is to say, the interval between two adjacent centers is 0.08 a.u. for H-nuclei and 0.07 a.u. for D- and T-nuclei²². For heteronuclear isotopologues, similar basis sets are used, except that the one (HD and DT) or two (HT) outermost off-centered pairs of orbital sets around the heaviest nucleus are suppressed and in compensation, one or two extra pairs of orbital sets are added to the lightest nucleus. So, in the homonuclear case, the electronic basis sets that were denoted: [cc-pV5Z + 16 (2s)] in our previous study²² are denoted [cc-pV5Z + 8 (2s) + 8 (2s)] in this paper, while the HD and DT basis sets are noted [cc-pV5Z + 10 (2s) + 6 (2s)], and the HT basis set is denoted by [cc-pV5Z + 12 (2s) + 4 (2s)]. This use of different basis sets is justified because in the center-of-nuclear-mass frame, the amplitude of the

vibrational motion of the light nucleus is more important than that of the heavy nucleus. Concretely, the absolute value of the coefficient of the unique vibrational coordinate Q in the sum over nuclei of Eq.(11) is two (respectively three) times smaller for D (respectively for T) than for H, in HD (respectively HT) see last line of Eq.(14) in²². So, for a given vibrational amplitude, (typically $Q_{max} \approx \sqrt{\frac{n+\frac{1}{2}}{\mu\omega}}$ in the harmonic approximation, where n is vibrational quantum number, μ the reduced mass, ω the angular frequency), the heavy nucleus deviates from its reference position along the internuclear axis two or three times less than the H nucleus, in HD and HT respectively. (For DT the ratio is two to three). In HT, to reduce the linear dependencies introduced by the 12 sets of off-centered orbitals on the H-side, a larger stepsize of 0.09 au between adjacent sets has been used. The chosen basis sets are not optimal to minimize ground state (GS) energies but they constitute good compromises to obtain ground and first excited states with similar accuracy, and get reasonably accurate first transition energies.

In addition to the electron-nucleus correlation energy, Eq.(3), we define the following interesting quantity:

$$E_{E-FCI}^{opt-MF} = E_{E-FCI}^{(CV)} - E_{E-FCI}^{(0)} \quad (16)$$

that we tentatively call the E-FCI-optimized mean field energy. Tables I and II show the convergence of the EN-SCFCI iterative process for respectively the homonuclear and heteronuclear isotopologues of dihydrogen. The step 0 E-FCI and the converged results permit to compute the E_{E-FCI}^{opt-MF} values displayed in Tab. III. We also provide in the last line of tables I and II the EN-FCI energies, which permit to compute the E_{correl}^{EN} values displayed in Tab. III.

The electronic correlation energy, Eq.(1), is given in Tab. III for the step 0 Hamiltonian (Coulomb attraction integrals smeared by the initial guess Kratzer fundamental basis function),

$$E_{correl}^{el} = E_{E-FCI}^{(0)} - E_{HF}^{(0)} \quad (17)$$

so that,

$$E_{EN-FCI}^{EN} - E_{HF}^{(0)} = E_{correl}^{el} + E_{E-FCI}^{opt-MF} + E_{correl}^{EN}. \quad (18)$$

This decomposition of the energy corrections with respect to $E_{HF}^{(0)}$ is somewhat arbi-

trary, since it depends upon the step 0, guess, nuclear function. A more meaningful decomposition is,

$$E_{EN-FCI}^{EN} - E_{HF}^{(CV)} = E_{correl}^{el} + E_{E-FCI}^{opt-MF} - E_{HF}^{opt-MF} + E_{correl}^{EN}, \quad (19)$$

where, E_{HF}^{opt-MF} is the difference between the converged HF-optimized mean field energy, $E_{HF}^{(CV)}$, and the step 0, HF-energy,

$$E_{HF}^{opt-MF} = E_{HF}^{(CV)} - E_{HF}^{(0)}, \quad (20)$$

because both E_{EN-FCI}^{EN} and $E_{HF}^{(CV)}$ are independent of the initial guess. However, the optimized mean-field energy differences, $(E_{E-FCI}^{opt-MF} - E_{HF}^{opt-MF})$, which can be calculated from Tabs. I and II, are quite small: 0.0000687 hartree for H₂. So, we will only discuss the three corrective terms with respect to $E_{HF}^{(0)}$ appearing in the right-hand side of Eq.(18). Note that, the latter quantity is a simpler reference in practice than $E_{HF}^{(CV)}$. To obtain the correction with respect to $E_{HF}^{(CV)}$ appearing in the right-hand side of Eq.(19), one just has to subtract an extra $E_{HF}^{opt-MF} \simeq E_{E-FCI}^{opt-MF}$ energy value.

The electronic correlation energy is only marginally sensitive to isotopic substitution, the largest difference between T₂ and H₂ being only of less than 54 μ hartrees. This is not surprising since the two-electron operator at the origin of electronic correlation is the same for all isotopologues. Note that the non-diagonal mass polarization term appearing in the last term on the right-hand side of Eq.(9) has been neglected in all calculations. So differences between isotopologues is an indirect effect arising from one-electron operators: the electronic kinetic operator which depends upon electron reduced mass, and the electron-nuclear attraction which depends upon the guessed fundamental vibrational function. The two effects should go in the same direction: the lighter the isotopologues, the smaller the reduced mass, the larger the electronic kinetic energy operator (which is positive), and at the same time, the more smeared the electron-nuclear attraction, the less negative the one-electron Coulomb potential. However, in fact, the electron reduced mass effect is negligible, and the two one-electron contributions vary in opposite directions: the electron-nuclear attraction being smeared, the electron density is less concentrated in the close neighbourhood of the nuclei where the electronic kinetic energy is the largest. So the electron-nuclear attraction is less negative as the mass is lighter

and the electronic kinetic energy is less positive at the same time. The electron-electron repulsion also benefits from the less concentrated electron density and is less positive for lighter isotopologues. Similar observations were made by Aguirre et al. on $[\text{He-H-He}]^+$ and isotopologues³⁴. However, these effects are observed at both the HF and FCI levels. The electronic correlation energy results from the difference between these effects at the two levels of calculation. As in the clamped nuclei at equilibrium geometry calculation, the signs of the one-electron contributions to the electronic correlation energy are preserved, that is to say, the electron-nuclear attraction gives a negative contribution while the kinetic energy a positive one. The electron-electron repulsion contribution remains negative and is the largest of the three. However, it is almost insensitive to nuclear mass. The absolute value of the sum of the three contributions diminishes as nuclear mass increases, showing that the electron-nuclear attraction effect is dominant, but it is a very small isotopic effect as already noted.

The SCF-optimized MF energies in Tab. III are one order of magnitude smaller than the electronic correlation energies. Yet, there are not negligible. The electron-nucleus correlation energies are more than a factor two larger. Both quantities have a much more significant variation with isotopic mass than the electron-electron correlation energies. These variations are closely related to those of the GS nuclear energy levels.

As can be anticipated from Tab. III and as depicted in Fig. 2 (upper panel), where the masses of fictitious hydrogen-like nuclei are varied, the quantity E_{correl}^{el} tends as $\frac{a}{\sqrt{M}}$ towards its clamped nuclei limit at the equilibrium geometry. This is explained by the fact that the ground state vibrational function of step 0 tends towards a Dirac delta distribution centered at the minimum of the Kratzer potential energy curve (PEC) (see Appendix). Therefore the electronic effective Hamiltonian of step 0 tends towards the clamped nuclei Hamiltonian at precisely this geometry²². The convergence behaviour as $\frac{1}{\sqrt{M}}$ is dictated by the rate of convergence of the Kratzer GS energy which can be shown to converge to the minimum energy value of the PEC as $\sqrt{\frac{D_e}{2\mu r_e^2}} = \frac{\sqrt{D_e}}{r_e} \times \frac{1}{\sqrt{M}}$.

For the same reason, E_{correl}^{EN} in Fig. 2 (lower panel) tends to zero as $\frac{1}{\sqrt{M}}$ when nuclear masses go to infinity. The equilibrium distance corresponding to the minimum

of the effective potential for nuclear motion might be different than that of the initial Kratzer PEC. However, at the clamped nuclei limit, the energy level will go down to this minimum and the total wave function will tend to a Hartree product of the clamped nuclei electronic eigenfunction with a nuclear Dirac distribution. Consequently, there will be no electron-nucleus correlation according to our definition. Let us recall that, the MF PEC is expected to have actually a deeper minimum than that of the BO PEC^{3,22}. One expects the electronic mean field potential energy for nuclear motion to be only accurate in the vicinity of the reference geometry, (which is usually chosen close to the equilibrium geometry). So, the closer to the limit of the clamped nuclei at the equilibrium geometry, the more effective the mean field approach. Note, by the way, that the number of iterations necessary for the EN-SCFCI process to converge (not reported here), decreases with increasing nuclear mass. For $M = 100$ amu only 3 iterations and for $M = 1000$ only 1 iteration were necessary.

Regarding the E-FCI-optimized mean field energy, E_{E-FCI}^{opt-MF} , we witness the same behaviour in $\frac{1}{\sqrt{M}}$ when M goes to infinity, (see Fig. 2 lower panel). However, its explanation is less straightforward, since after step 0, the nuclear wave function will be *a priori* a linear combination of Kratzer potential eigenfunctions: for $l > 0$, $\phi_0^{(2l)}(Q) = \sum_{i=0}^{N_{kra}-1} c_i \phi_i^{Kratzer}(Q)$, (with $N_{kra} = 16$ in our calculations). The Kratzer eigenfunction, $\phi_i^{Kratzer}$ has $i + 1$ peaks and i nodes. As the mass goes to infinity, $\phi_i^{Kratzer}$ will tend to a sum of $i + 1$ delta distributions. So, the effective potential seen by the electrons at step $(2l + 1)$ will tend to a weighted sum of point charges Coulomb potentials (with weights related to the c_i^2 's, to the number of peaks and to their relative heights in a given Kratzer eigenfunction). More precisely, there will be two point-charges at the equilibrium positions of the two nuclei corresponding to the peaks of $\lim_{\mu \rightarrow \infty} \phi_0^{Kratzer}$ (with weight c_0^2) and many others located apart from the latter according to the peaks of the $\lim_{\mu \rightarrow \infty} \phi_i^{Kratzer}$'s for ($i > 0$). However, we have observed in our calculations that the coefficient c_0 is largely dominant. It seems that the contributions of the minor peaks are small enough to preserve the location of the effective PEC minimum at the Kratzer reference geometry.

In comparing our E_{correl}^{EN} results with those reported by other groups in Tab. III, care

must be taken that the reference “uncorrelated” functions are not exactly the same, that the nuclear motion coordinates and basis sets are different and that the correlation treatment can also be different (case of Ref.¹⁹). Our E_{correl}^{EN} absolute values are about 50% larger than the NOMO-MP2 values reported by Nakai¹⁹ after approximate removal of translations and rotations. Their electronic correlation absolute values, in the order of 0.032 hartree, are also smaller than ours. This is partly explained by the smaller size of the basis sets (electronic and nuclear) used in the NOMO calculations and partly by the level of correlation treatment. If we transfer the coupled cluster BD-MP2 differences found in¹⁵ without translation and rotation removal, to the NOMO-MP2 results with translation and rotation removal of¹⁹, we almost recover the 50% discrepancy.

Conversely, the E_{correl}^{EN} absolute values obtained for H₂ and D₂ by the MCMO-Full CI method with a [5s2p1d] electronic basis set and a [1s1p1d] Gaussian-Type function nuclear basis set are about twice too large²⁰. The electronic correlation absolute values are in the order of 0.038 hartree. Clearly, the larger basis sets used, enable one to recover more correlation energies. However, we strongly suspect that the factor 2 observed is due to the fact that the correlated motion of the nuclei is counted twice, despite the elimination of translations and rotations. This is supported by the case of HD: if added, the proton and deuteron-nucleus E_{correl}^{EN} values give an electron-nucleus correlation energy twice too large. In contrast, their mean value is very close to our result.

V. CONCLUSION

In this paper we have introduced a definition of electron-nucleus correlation energy inspired from the quantum chemical definition of electronic correlation. In contrast with previous works¹⁵⁻¹⁹, our reference “electron-nucleus” uncorrelated wave function is a Hartree product of FCI-type wave functions. So, electron-electron correlations as well as nuclear motion correlations are properly eliminated at any level of post-Hartree product electron-nucleus calculations. In addition, the use of internal coordinates for nuclear motion prevents contamination from translational and rotational motions.

We have shown that the EN-MFCI method was the appropriate method to calculate the lowest electron-nucleus correlation-free energy. In ref.¹⁵, it was found at the NOMO

coupled-cluster level that reoptimization of the one-particle functions was necessary to account correctly for electron-nucleus correlation. However, this sensitivity to the choice of one-particle functions can be bypassed for small enough systems, by using the EN-FCI wave function. Then, the exact electron-nucleus correlation energy within a given one-particle basis set can be evaluated.

Numerical applications to the dihydrogen isotopologues have shown that it is a significant quantity even for the heaviest isotopologue, T₂. However, it decreases with nuclear mass unlike electronic correlation energy. For T₂, it is almost an order of magnitude smaller than the electronic correlation energy. It is expected to increase with nuclear charge for heavier atoms than hydrogen, but then the number of electrons and the electronic correlation energy will increase accordingly.

This rises the question of the best strategy to approximate total molecular wave functions. Should one approximate electron-nucleus correlation as done implicitly by using the Born-Oppenheimer ansatz, and then try to approximate electronic correlation by some post-Hartree-Fock method within the BO framework? Our results suggest a less conventional strategy. Since the electronic correlation energy is the largest quantity, one should attempt to recover it first. Then, one would deal with the electron-nucleus correlation energy. This is precisely the spirit of the EN-MFCI approach.

APPENDIX A: ELECTRON-NUCLEUS COUPLING AND ELECTRON-NUCLEUS CORRELATION

Electron-nucleus coupling and electron-nucleus correlation are two different notions. The existence of an electron-nucleus coupling term in the Hamiltonian is a necessary condition for electron-nucleus correlation. However, it is not sufficient: consider a Hamiltonian $H = H_N + H_e + H_{eN}$, with nuclear Hamiltonian, $H_N = \sum_i E_i^N |\Psi_i^N\rangle\langle\Psi_i^N| \otimes Id_e$, electronic Hamiltonian, $H_e = \sum_j E_j^e Id_N \otimes |\Psi_j^e\rangle\langle\Psi_j^e|$, and coupling term, $H_{eN} = \sum_{i,j} E_{i,j}^{eN} |\Psi_i^N \otimes \Psi_j^e\rangle\langle\Psi_i^N \otimes \Psi_j^e|$. The identity of the nuclear motion (respectively, electronic) Hilbert space can be written, $Id_N = \sum_i |\Psi_i^N\rangle\langle\Psi_i^N|$ (respectively, $Id_e = \sum_j |\Psi_j^e\rangle\langle\Psi_j^e|$). So, the total Hamiltonian will be diagonal in the product basis of electronic and nuclear eigenfunctions, $H = \sum_{i,j} (E_i^N + E_j^e + E_{i,j}^{eN}) |\Psi_i^N \otimes \Psi_j^e\rangle\langle\Psi_i^N \otimes \Psi_j^e|$. The coupling term will not be negligible if $E_{i,j}^{eN} \approx (E_i^N + E_j^e)$. However, there will be no electron-nucleus

correlation in this case according to our definition.

However, electron-phonon coupling is still a debated issue in condensed matter^{35,36}. Toys model could be studied in the frame of the EN-MFCI method to assess the approximations done in this field.

APPENDIX B: CLAMPED NUCLEI LIMIT

This appendix provides some details on the limit of large nuclear masses. At step 0, we start from a ground state (GS) Kratzer PEC wave function to build the effective electronic Hamiltonian. Its non-constant factor, in adimensional coordinate, behaves as $x^\lambda \times \text{Exp}[-(\lambda - 1)x]$. The coefficient λ grows as $\sqrt{\mu}$ as μ goes to ∞ . Hence the GS function at a given x is dominated by $\text{Exp}[-\lambda(x - \text{Ln}[x])]$. The function $f(x) := (x - \text{Ln}[x])$ is positive on $]0, +\infty[$, in fact, it reaches a minimal value of 1 at $x = \frac{x}{r_e} = 1$ i.e. at the minimum of the Kratzer PEC. So, the unnormalized GS wave function tends to 0 for all x . However, because of the constraint that the square of its module must integrate to 1, the normalized GS eigenfunction becomes sharply peaked, and eventually tends to a Dirac distribution centered at r_e . This is illustrated in Fig. 3.

At later steps, the effective potential for nuclear motion might be different, but as long as it has a bound state in a single minimum, one expects the same behavior: the energy level will descend to the effective PEC minimum and the GS eigenfunction will concentrate into a Dirac distribution centered at this minimum.

As we have seen in our previous article²², such a delta function will result in an effective electronic Hamiltonian, at the next step, that is nothing but the usual Clamped Nuclei hamiltonian at the minimum geometry.

ACKNOWLEDGEMENTS

The research of this work was supported by grants from the National Natural Science Foundation of China (Project Nos. 21203147, 21273011, and 21290192) as well as Beijing National Laboratory for Molecular Sciences. One author (PCC) acknowledges the JAD laboratory for providing computer facilities, and support from the grant CARMA ANR-

12-BS01-0017. This work was granted access to the HPC and visualization resources of the “Centre de Calcul Interactif” hosted by University Nice Sophia Antipolis.

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TABLES

iteration number	H_2		D_2		T_2	
	HF	Full CI	HF	Full CI	HF	Full CI
0	-1.1100467	-1.1508083	-1.1167995	-1.1575238	-1.1198084	-1.1605164
1	-1.1138025	-1.1546101	-1.1195670	-1.1603205	-1.1221191	-1.1628484
2	-1.1139342	-1.1547108	-1.1196533	-1.1603841	-1.1221867	-1.1628971
3	-1.1139687	-1.1547212	-1.1196775	-1.1603892	-1.1222067	-1.1629007
4	-1.1139925	-1.1547273	-1.1196943	-1.1603926	-1.1222208	-1.1629030
5	-1.1140094	-1.1547317	-1.1197066	-1.1603949	-1.1222308	-1.1629043
6	-1.1140215	-1.1547349	-1.1197148	-1.1603967	-1.1222379	-1.1629055
7	-1.1140300	-1.1547374	-1.1197209	-1.1603978	-1.1222430	-1.1629067
8	-1.1140360	-1.1547391	-1.1197252	-1.1603988	-1.1222467	-1.1629073
9	-1.1140404	-1.1547403	-1.1197283	-1.1603993	-1.1222493	-1.1629076
CV	-1.1140507	-1.1547436	-1.1197358	-1.1604013	-1.1222556	-1.1629091
EN-FullCI GS energy	-1.1638438		-1.1669493		-1.1683018	

TABLE I. Convergence of homonuclear H_2 -isotopologue ground state energy (hartree) with MFCI iterations for different electronic methods: Hartree-Fock (HF) and Full configuration interactions (Full CI). The $[\text{cc-pV5Z} + 8(2s) + 8(2s)] \otimes [16 \text{ Kratzer}]$ basis has been used. The vibrational method is always the Full CI. CV stands for “converged”. The EN-FullCI GS energy in hartrees is also provided.

iteration number	HD		HT		DT	
	HF	Full CI	HF	Full CI	HF	Full CI
0	-1.1126978	-1.1534303	-1.1133192	-1.1540316	-1.1180947	-1.1588075
1	-1.1162698	-1.1570198	-1.1169062	-1.1576418	-1.1206905	-1.1614377
2	-1.1163184	-1.1570319	-1.1169507	-1.1576530	-1.1207725	-1.1614926
3	-1.1163428	-1.1570377	-1.1169732	-1.1576578	-1.1207942	-1.1615006
4	-1.1163554	-1.1570406	-1.1169851	-1.1576605	-1.1208094	-1.1615014
5	-1.1163619	-1.1570423	-1.1169915	-1.1576619	-1.1208203	-1.1615019
6	-1.1163652	-1.1570433	-1.1169948	-1.1576627	-1.1208281	-1.1615028
7	-1.1163669	-1.1570437	-1.1169966	-1.1576632	-1.1208337	-1.1615034
8	-1.1163678	-1.1570439	-1.1169975	-1.1576635	-1.1208378	-1.1615041
9	-1.1163683	-1.1570441	-1.1169980	-1.1576636	-1.1208406	-1.1615047
CV	-1.1163687	-1.1570441	-1.1169985	-1.1576637	-1.1208478	-1.1615062
EN-FullCI GS energy	-1.1652867		-1.1658175		-1.1675974	

TABLE II. Convergence of heteronuclear H₂-isotopologue ground state energy (hartree) with MFCI iterations for different electronic methods: Hartree-Fock (HF) and Full configuration interactions (Full CI). The [cc-pV5Z + 10 (2s)+ 6 (2s)] \otimes [16 Kratzer] basis has been used for HD and DT, while [cc-pV5Z + 12 (2s)+ 4 (2s)] \otimes [16 Kratzer] has been used for HT. The vibrational method is always the Full CI. CV stands for “converged”. The EN-FullCI GS energy in hartrees is also provided.

	H₂	HD	HT	D₂	DT	T₂
EE	0.0407616	0.0407325	0.0407125	0.0407243	0.0407128	0.0407080
MF	0.0039353	.0036139	0.0036321	0.0028775	0.0026987	0.0023927
EN (This work)	0.0091002	0.0082426	0.0081537	0.0065480	0.0060912	0.0053927
EN (Ref. ¹⁹)	0.006452	N/A	N/A	0.004583	N/A	0.003809
EN (Ref. ²⁰)	0.0194298	^{0.0115312(H)} _{0.0063633(D)}	N/A	0.0137057	N/A	N/A
BO Δ_{ZPE}	.0099298	.0086146	.0081276	.0070466	.0064388	.0057658
EN-FullCI $\nu : 0 \rightarrow 1$	4165	3636	3439	2994	2744	2465

TABLE III. Comparison of absolute values of electron-electron, optimized mean-field and electron-nucleus correlation energies in hartrees. (All these quantities are actually negative). The TR₀F-NOMO/MP2 EN-values of Ref.¹⁹ and the Trans(-)Rot(-)-MCMO/Full-CI EN-values of Ref.²⁰ are provided, when available. For HD, the proton and deuteron correlation energies of Ref.²⁰ are given one on the top of the other. The clamped nuclei EE absolute value is 0.0406384 hartree. The BO ZPE correction in hartrees and the EN-FCI fundamental transition wave number (in cm⁻¹) between the ground and first excited states are also provided.

FIGURES

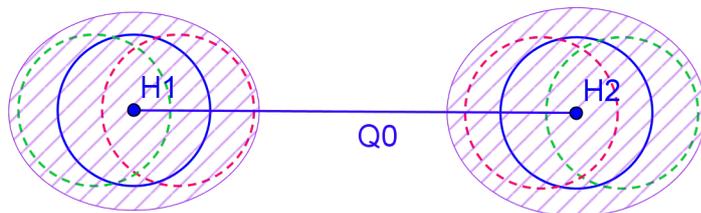


FIG. 1. Schematic representation of the smeared electronic density in H₂. The electronic density at the equilibrium distance, Q_0 (blue ring), is convoluted with the vibrational motion. When the molecule contracts or extends itself, the electronic density is displaced accordingly (dashed red and green rings). So the fixed electronic orbital basis set must be able to represent a smeared density (hatched purple ellipse) in particular a smeared core electron density.

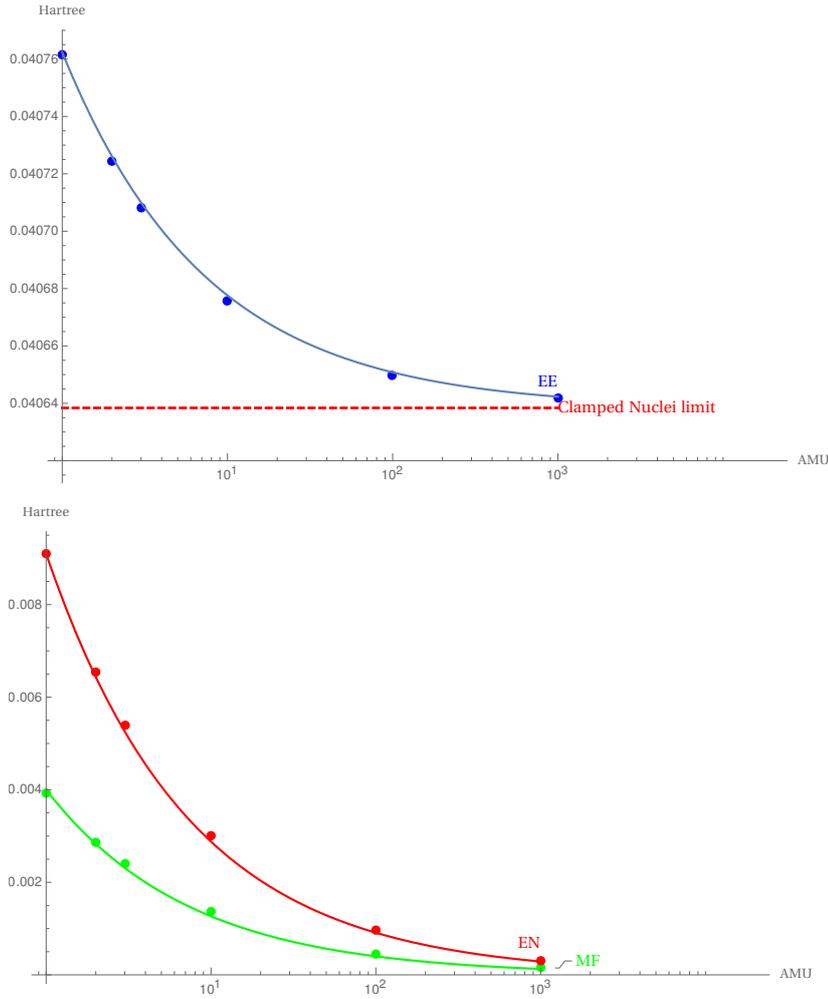


FIG. 2. Absolute values of correlation energies versus nuclear masses for (X^+, X^+, e^-, e^-) systems, X being a proton-like nucleus of arbitrary mass. Upper panel: the blue dots are the computed electron-electron correlation energy absolute values, the blue line is a fitted curve of the form $\frac{a}{\sqrt{M}} + b$ (M being the abscissa, $b = .0406384$ the clamped nuclei value, $a = 0.000124$), the red dashed line represents the clamped nuclei asymptote. Lower panel: the red (resp. green) dots are the computed electron-nuclear correlation (resp. SCF-optimized mean field) energy absolute values, the lines are fitted curves of the form $\frac{a}{\sqrt{M}}$ ($a = 0.004$ for the green curve and $a = 0.0091$ for the red one). The stepsize for the positioning of the off-centered basis orbitals is 0.08 au for H_2 , and 0.07 au in all other calculations (smaller stepsizes result in linear dependencies in the molecular orbital basis sets and higher electronic energies).

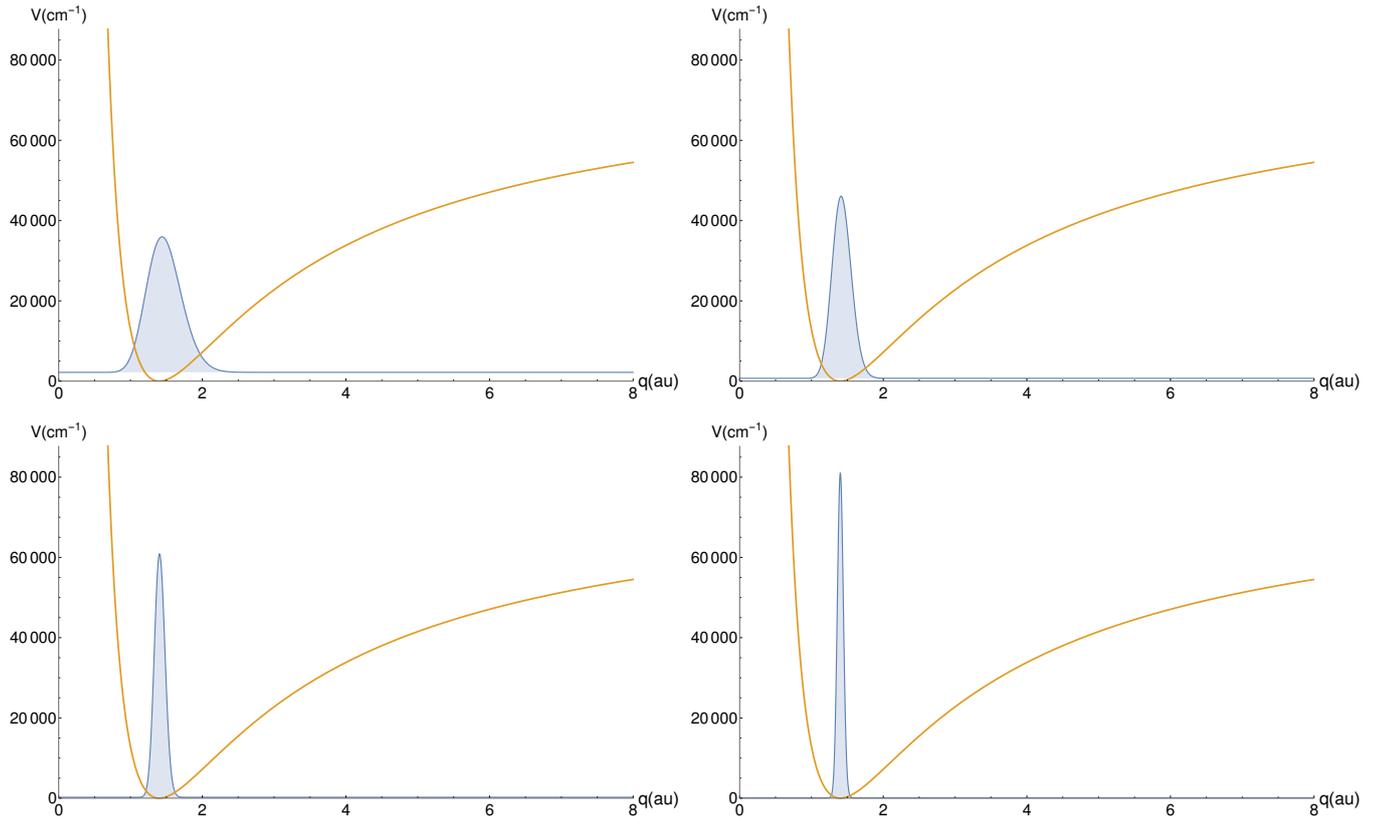


FIG. 3. Kratzer ground state wave function as reduced mass increases. The plots are for reduced masses of $1/2$, $10/2$, $100/2$, $1000/2$ atomic mass units, respectively. The Kratzer potential curve corresponds to the parameters used in our calculations.