On the physical interpretation of the nuclear molecular orbital energy

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Recently, several groups have extended and implemented molecular orbital (MO) schemes to simultaneously obtain wave functions for electrons and selected nuclei. Many of these schemes employ an extended Hartree-Fock approach as a first step to find approximate electron-nuclear wave functions and energies. Numerous studies conducted with these extended MO methodologies have explored various effects of quantum nuclei on physical and chemical properties. However, to the best of our knowledge no physical interpretation has been assigned to the nuclear molecular orbital energy (NMOE) resulting after solving extended Hartree-Fock equations. This study confirms that the NMOE is directly related to the molecular electrostatic potential at the position of the nucleus. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984098>]

I. INTRODUCTION

In recent decades, several theoretical approaches have been developed to treat selected nuclei on the same footing of electrons in molecular orbital electronic structure methods. Some examples of these methods are the multicomponent molecular orbital (MC-MO) method,^{1,2} the nuclear orbital plus molecular orbital (NOMO) method,^{3,4} the nuclear-electronic orbital (NEO) approach,⁵ and the any particle molecular orbital (APMO) approach.⁶ One advantageous feature of these nuclear molecular orbital (NMO) approaches over their electronic structure counterparts is that nuclear quantum effects (NQE) on molecular properties can be introduced directly in NMO calculations and not as further corrections. Regularly, NMO methods have been applied to study nuclear mass and delocalization effects on electronic properties,^{7–10} internuclear distances,^{11–13} infrared spectra,^{7,14,15} NMR spectra shifts,^{16–19} and isotope effects.^{20–23} Most of these studies have considered hydrogen nuclei quantum mechanically and heavier nuclei as point charges under the Born-Oppenheimer (BO) approximation. It is now well established that NMO methods recurrently overestimate NQEs.^{24–26} Still, hydrogen isotope effects on molecular properties calculated with NMO methods display correct trends with respect to the variation of the nuclear mass.^{4,6,13,20,26,27}

Additional NMO studies have further investigated nuclear delocalization in terms of the analysis of nuclear wave functions and their associated vibrational frequencies,^{24,26,28–30} obtained as the difference of two nuclear molecular orbital energies. The results of these investigations regularly exhibit severe deviations from experimental data and other theoretical results based on the BO approximation. These studies have concluded that the main source of deviation is either the lack or the incomplete description of nuclear-electron correlation, emerging in NMO methods between quantum nuclei and electrons. This is undoubtedly the main source of criticism towards NMO methods.^{27,31}

Surprisingly, despite all the efforts made to improve the accuracy and resolve many theoretical and computational

challenges emerging from the use of NMO methods, little attention has been paid to providing a physical interpretation to the nuclear molecular orbital energies (NMOEs) that result by solving the nuclear Fock equations in the NMO-Hartree-Fock (NMO-HF) method.

Thus, the main goal of this contribution is to show a physical interpretation to these NMOEs. A first step in this direction involves manipulating the expression of an occupied NMO in the NMO-HF method and associating it to the ionization energy of the quantum nucleus, assuming there is no electronic nuclear relaxation. This brings us to Koopmans' theorem (KT) for quantum nuclei. This extended KT is not new;³² in fact, we have recently employed it in an attempt to predict ionization energies of protons (i.e., proton binding energies, PBEs).^{33–35} These studies concluded that contrary to electron KT, nuclear KT performs poorly in the prediction of PBEs.

As a second step, we derive the expressions of the NMOE and the nuclear ionization energy and contrast them with the definition of the molecular electrostatic potential (MEP). This analysis permitted us to establish a direct connection between the NMOE and the MEP.

As a final step, we perform numerical tests that expose that the NMOEs coming from NMO-HF calculations can be employed to estimate the MEPs at the average positions of the nuclei in regular BO Hartree-Fock (BO-HF) calculations.

Surprisingly, this novel interpretation of the NMOEs as MEPs at nuclei opens up new possibilities for APMO-HF calculations, since calculated MEPs at nuclei have been employed to predict molecular properties,^{36–45} and chemical reactivity.^{46–49}

II. THEORETICAL AND COMPUTATIONAL ASPECTS

A. Theory

At the Hartree-Fock (HF) level of theory, the energy required to remove nucleus Q from the molecular system with N_N nuclei, E_Q , in a process that neglects electron and nuclear

relaxations, can be calculated as

$$E_Q = E_{N_N} - E_{N_C} = - \sum_m^{N_e} Z_Q \int \frac{|\chi_m(r)|^2}{|r - r_Q|} dr + \sum_I^{N_C} \frac{Z_I Z_Q}{r_{IQ}}. \quad (1)$$

Here, for convenience we separate nucleus Q from the remaining N_C nuclei, where $N_C = N_N - 1$.

On the other hand, the MEP,⁵⁰ $V(r_Q)$, produced by N_e electrons and N_C nuclei at point r_Q occupied by nucleus Q is

$$V(r_Q) = - \int \frac{\rho^e(r)}{|r - r_Q|} dr + \sum_I^{N_C} \frac{Z_I}{r_{IQ}}, \quad (2)$$

$$= - \sum_m^{N_e} \int \frac{|\chi_m(r)|^2}{|r - r_Q|} dr + \sum_I^{N_C} \frac{Z_I}{r_{IQ}}. \quad (3)$$

Contrasting Eqs. (1) and (3), we find that

$$E_Q = V(r_Q) \cdot Z_Q. \quad (4)$$

This equation exposes that $V(r_Q)$ can be utilized as a first estimate of the binding energy of point-charge nucleus Q at point r_Q .

Now consider a molecular system with N_e electrons and N_N nuclei in which both electrons and nucleus Q are treated quantum mechanically, with the APMO approach, while the remaining N_C nuclei are considered as point charges under the BO approximation.

At the APMO Hartree-Fock (APMO-HF) level of theory,⁶ the total wave function, Ψ_0 , is approximated as a product of a single configurational electronic wave function, Ψ^e , and a nuclear molecular orbital, ϕ^Q ,

$$\Psi_0 = \Psi^e \cdot \phi^Q. \quad (5)$$

Here, Ψ^e and ϕ^Q are obtained by solving simultaneously Hartree-Fock equations for electrons

$$f^e \chi_i = \epsilon_i^e \chi_i, \quad i = 1, \dots, N_e, \quad (6)$$

$$f^e(i) = -\frac{\nabla_i^2}{2} - \sum_J^{N_C} \frac{Z_J}{r_{IJ}} + \sum_j^{N_e} [J_j^e(i) - K_j^e(i)] - Z_Q J^Q(i), \quad (7)$$

and for the quantum nucleus Q

$$f^Q \phi^Q = \epsilon^Q \phi^Q, \quad (8)$$

$$f^Q(I) = -\frac{\nabla_I^2}{2M_Q} + \sum_J^{N_C} \frac{Z_J Z_Q}{r_{IJ}} - Z_Q \sum_{i=1}^{N_e} J_i^e(I). \quad (9)$$

In Eq. (7), $J_j^e(i)$ and $K_j^e(i)$ are the regular electronic Coulomb and exchange operators, respectively, and $J^Q(i)$ and $J_i^e(I)$ are the Coulomb operators between nuclei and electrons, respectively.

Electronic, ϵ_m^e , and nuclear, ϵ^Q , orbital energies in Eqs. (6) and (8) are given by

$$\begin{aligned} \epsilon_m^e &= \langle m | f^e | m \rangle \\ &= -\frac{1}{2} \langle m | \nabla^2 | m \rangle - \sum_I^{N_C} Z_I \int \frac{|\chi_m(r)|^2}{|r - r_I|} dr + \sum_n^{N_e} \langle mn | mn \rangle \\ &\quad - Z_Q \iint \frac{|\phi^Q(r_Q)|^2 |\chi_m(r)|^2}{|r - r_Q|} dr dr_Q, \end{aligned} \quad (10)$$

$$\begin{aligned} \epsilon^Q &= \langle \phi^Q | f^Q | \phi^Q \rangle \\ &= -\frac{\langle \phi^Q | \nabla^2 | \phi^Q \rangle}{2M_Q} + Z_Q \sum_I^{N_C} Z_I \int \frac{|\phi^Q(r_Q)|^2}{|r_I - r_Q|} dr_Q \\ &\quad - Z_Q \sum_m^{N_e} \iint \frac{|\phi^Q(r_Q)|^2 |\chi_m(r)|^2}{|r - r_Q|} dr dr_Q. \end{aligned} \quad (11)$$

If electron and nuclear relaxations occurring upon the detachment of nucleus Q are neglected, the energy associated with the detachment of nucleus Q , E_Q^{APMO} , can be calculated as

$$\begin{aligned} E_Q^{APMO} &= E_{N_N}^{APMO} - E_{N_C}^{APMO} \\ &= -\frac{\langle \phi^Q | \nabla^2 | \phi^Q \rangle}{2M_Q} + Z_Q \sum_I^{N_C} Z_I \int \frac{|\phi^Q(r_Q)|^2}{|r_I - r_Q|} dr_Q \\ &\quad - Z_Q \sum_m^{N_e} \iint \frac{|\chi_m(r)|^2 |\phi^Q(r_Q)|^2}{|r - r_Q|} dr dr_Q. \end{aligned} \quad (12)$$

Simple inspection of Eqs. (11) and (12) shows that

$$\epsilon^Q = E_Q^{APMO}. \quad (13)$$

Thus, ϵ^Q is the energy for binding or detaching ($-\epsilon^Q$) quantum nucleus Q when electron and nuclear relaxations are neglected. This is no other than an extended Koopmans' theorem for quantum nuclei. Reyes and coworkers utilized ϵ^Q data of numerous molecular systems as first estimates of proton binding energies (PBEs).^{33,34} They contrasted their PBEs with experimental data finding errors in their predictions over 80%. They concluded that ϵ^Q 's cannot be interpreted as PBEs and also that the main source of error in these calculations was the neglect of electronic and nuclear relaxations after proton detachment.

In a different attempt to find a physical interpretation to ϵ^Q , we follow the same line of thought connecting E_Q and $V(r_Q)$ in Eqs. (1) and (3). There, $V(r_Q)$ is associated with the binding energy of a positive point charge $Z = 1$ to the molecule at point r_Q . However, if the charge is defined by a charge density, $|\phi^Q|^2$, its binding energy can be estimated in terms of the expectation value of $V(r_Q)$, $\langle V(r_Q) \rangle$ (also referred to as the averaged MEP or AMEP)

$$\begin{aligned} \langle V(r_Q) \rangle &= \langle \phi^Q | V(r_Q) | \phi^Q \rangle \\ &= - \sum_i^{N_e} \iint \frac{|\chi_i(r)|^2 |\phi^Q(r_Q)|^2}{|r - r_Q|} dr dr_Q \\ &\quad + \sum_I^{N_C} Z_I \int \frac{|\phi^Q(r_Q)|^2}{|r_I - r_Q|} dr_Q \end{aligned} \quad (14)$$

Contrasting the above equation with Eqs. (12) and (13), we find

$$\begin{aligned} \epsilon^Q &= -\frac{\langle \phi^Q | \nabla^2 | \phi^Q \rangle}{2M_Q} + Z_Q \cdot \langle V(r_Q) \rangle \\ &= -k^Q + Z_Q \cdot \langle V(r_Q) \rangle. \end{aligned} \quad (15)$$

Solving for $\langle V(r_Q) \rangle$, we obtain

$$\langle V(r_Q) \rangle = \frac{\epsilon^Q + k^Q}{Z_Q}. \quad (16)$$

This equation exposes that the expectation value of the MEP, $\langle V(r_Q) \rangle$, at position r_Q can be estimated from ϵ^Q and the kinetic energy (KE) of nucleus Q , k^Q . To confirm the validity of this equation in the calculation of the MEP, we will contrast the $\langle V(r_Q) \rangle$ with the $V(r_Q)$ derived from BO-HF calculations. To that aim, we perform APMO-HF single point calculations on a diverse set of molecular systems containing quantum nuclei with atomic numbers Z_Q ranging from 1 to 18.

B. Computational aspects

Single point APMO-HF calculations were performed on 75 organic and inorganic molecules selected to cover a wide range of chemical diversity. This set comprises nuclei with atomic numbers, Z , ranging from 1 to 18 (Table S1 of the [supplementary material](#)). Calculations considered all nuclei quantum mechanically resulting in a set of 512 quantum nuclei. These calculations were performed with the LOWDIN package⁵¹ employing molecular geometries optimized at the HF/6-311G and HF/6-311++G(d,p) levels with the GAMESS code.⁵² The resulting ϵ^Q 's and kinetic energies were replaced in Eq. (16) to obtain the corresponding $\langle V(r_Q) \rangle$. The MEP at nucleus Q , $V(r_Q)$, is calculated with Eq. (3), where r_Q is the expectation value of nuclear position at the APMO/HF level.

In addition, we explored the dependence of the AMEPs on the choice of electronic/nuclear basis sets. To that aim, we analyzed the results of these basis set combinations: 6-311G/7s, 6-311G/7s7p7d, 6-311++G(d,p)/7s, and 6-311++G(d,p)/7s7p7d. The exponents of the nuclear basis sets 7s and 7s7p7d are determined by the even-tempered scheme reported by Nakai and collaborators.^{3,53}

III. RESULTS AND DISCUSSION

Here, we are interested in answering the question of whether a ϵ^Q obtained from a APMO-HF single point calculation can be used to predict the MEP at nucleus Q . For this purpose, we first insert ϵ^Q and nuclear kinetic energy data in Eq. (16) to obtain the corresponding AMEPs, $\langle V(r_Q) \rangle$. These AMEPs are later contrasted with the corresponding MEPs calculated employing Eq. (4) and the electronic wave function of the corresponding APMO-HF calculation.

Figure 1(a) plots the AMEPs of the set of 512 nuclei along with their corresponding MEPs. These calculations

TABLE I. Correlation parameters of $\langle V(r_Q) \rangle$ vs $V(r_Q)$ and $\frac{\epsilon^Q}{Z_Q}$ vs $V(r_Q)$ for 512 nuclei, using four combinations of electronic and nuclear basis sets.

Basis set	$m * \langle V(r_Q) \rangle + b$			$m * \frac{\epsilon^Q}{Z_Q} + b$		
	m	b	R^2	m	b	R^2
6-311G/7s	1.0011	-0.0239	1.0000	1.0022	-0.0468	1.0000
6-311G/7s7p7d	1.0011	-0.0234	1.0000	1.0022	-0.0451	1.0000
6-311++G(d,p)/7s	1.0011	-0.0238	1.0000	1.0022	-0.0467	1.0000
6-311++G(d,p)/7s7p7d	1.0011	-0.0236	1.0000	1.0022	-0.0457	1.0000

employed the 6-311++G(d,p) electronic and 7s7p7d nuclear basis sets. This plot presents $R^2 = 1.0000$ and a slope = 1.0011 that clearly indicates the excellent correlation between the AMEPs and MEPs for this diverse set of nuclei. As observed, a MEP can be predicted from a AMEP employing the equation $V(r_Q) = 1.0011 \langle V(r_Q) \rangle - 0.0236$. Additional correlation parameters for the remaining combinations of the electronic/nuclear basis set reported in Table I also display excellent agreement.

We now inspect in more detail the performance of the AMEPs in the prediction of the MEPs for each type of nucleus. The linear regression parameters for each nucleus display R^2 and slopes in the ranges (0.9999, 1.0000) and (0.9971, 1.0017), respectively (Table S6 of the [supplementary material](#)). These results reconfirm that AMEPs obtained employing Eq. (16) can be used to properly predict the MEPs.

We now question whether the MEP at nucleus Q can be predicted directly from ϵ^Q .

To this aim, we plot ϵ^Q/Z_Q vs MEP in Fig. 1(b) for the set of 512 nuclei. As observed, this plot presents $R^2 = 1.0000$ and slope = 1.0022. This excellent correlation strongly suggests that a MEP on nucleus Q can be predicted from ϵ^Q employing the equation $V(r_Q) = 1.0022 \frac{\epsilon^Q}{Z_Q} - 0.0457$.

These results clearly suggest that the contribution of $\frac{k^Q}{Z}$ to $\frac{\epsilon^Q}{Z_Q}$ is small and as result $\langle V(r_Q) \rangle \approx \frac{\epsilon^Q}{Z_Q}$. To verify this, in Fig. 2 we plot $\frac{k^Q}{Z}$, $\frac{\epsilon^Q}{Z_Q}$, and $\langle V(r_Q) \rangle$ vs Z and list in Tables S2–S5 of the [supplementary material](#) these data for the whole set of molecules. As observed, for all systems considered the magnitude of $\frac{k^Q}{Z}$ is small confirming that $\frac{\epsilon^Q}{Z_Q}$ can be used as an alternative to $\langle V(r_Q) \rangle$.

FIG. 1. Correlation plots of (a) $\langle V(r_Q) \rangle$ vs $V(r_Q)$ and (b) $\frac{\epsilon^Q}{Z_Q}$ vs $V(r_Q)$ for a set of 512 nuclei containing H, Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, and Ar. Calculations were performed with the 6-311++G(d,p) electronic and 7s7p7d nuclear basis sets.

FIG. 2. Distribution of k^Q , ϵ^Q , and $\langle V(r_Q) \rangle$ for a set of 512 nuclei sorted by Z_Q . Calculations were performed with the 6-311++G(d,p) electronic and 7s7p7d nuclear basis sets.

Now, we analyze the performance of $\frac{\epsilon^Q}{Z_Q}$ in the prediction of the MEP by the type of nucleus. Linear regression parameters reported for each nucleus display R^2 and slopes in the ranges (0.9999, 1.0000) and (0.9971, 1.0047), respectively (Table S6 of the [supplementary material](#)). These results reconfirm that ϵ^Q can be used to properly predict the MEPs on nuclei.

Any observed discrepancy between the MEP calculated employing Eq. (4) and those derived from Eq. (16) and from $\frac{\epsilon^Q}{Z_Q}$ are brought about by the quantum description of nuclei in the APMO-HF approach. This can be interpreted as a manifestation of the effect of nuclear delocalization on the nuclear-nuclear and nuclear-electron interaction energies and the nuclear kinetic energy. Previous studies have concluded that a systematic increase of the mass of a nucleus, treated quantum mechanically within a NMO approach, will gradually localize the nucleus bringing NMO derived properties closer to those calculated with BO based methods.^{9,54,55} As a consequence, we expect that by gradually increasing the mass of nucleus Q , $\frac{\epsilon^Q}{Z_Q}$ and $\langle V \rangle$ will approach $V(r_Q)$. To test this conjecture, we increase systematically the mass of hydrogen nuclei in acetic acid. These calculations considered hydrogen nuclei mechanically and the remaining nuclei as point charges.

FIG. 3. Variation of $V(r_Q) - \langle V \rangle$ and $V(r_Q) - \frac{\epsilon^Q}{Z_Q}$ with respect to the nuclear mass of H in acetic acid.

Figure 3 plots the differences MEP-AMEP and $\text{MEP} - \frac{\epsilon^Q}{Z_Q}$ with respect to the nuclear mass. As anticipated, these differences approach zero in the infinite mass limit.

The results presented here confirm that ϵ^Q , either through the use of $\frac{\epsilon^Q}{Z_Q}$ or Eq. (16), can be utilized to predict MEPs on nuclei. The discrepancies in the MEPs obtained from a molecular orbital BO method and those obtained from ϵ_Q are associated with nuclear quantum effects introduced by the quantum description of nucleus Q .

IV. CONCLUDING REMARKS AND PERSPECTIVES

We derived an expression that uses ϵ^Q and the kinetic energy of nucleus Q to calculate the average MEP, $\langle V(r_Q) \rangle$. We contrasted the results of calculated AMEPs and MEPs of 512 nuclei finding excellent agreement between the data for all the combinations of electronic and nuclear basis sets considered. We additionally found that a MEP can be directly predicted from ϵ^Q . An analysis of the observed discrepancies between calculated AMEPs and MEPs is directly associated with the delocalized nature of the quantum nucleus. This was confirmed observing how the AMEPs come close to the MEPs as the mass of quantum nucleus was increased. The results presented in this work strongly suggest that ϵ^Q can be used as an alternative tool for calculating MEPs. An appealing feature of this scheme is that only one APMO-HF single point calculation is needed to obtain all the MEPs of a molecule. The computational scaling of the APMO-HF method is that of HF. Therefore, the applicability of the method is that of the HF method. As of today, the nuclear orbital energy, ϵ , has been mainly interpreted using the Koopmans theorem as a nuclear ionization energy, and it is known that it provides poor results with respect to experimental data. Consequently, this new physical interpretation of ϵ as a MEP opens new possibilities for NMO-HF calculations in other fields, i.e., the nuclear wave function can be used as an alternative tool for the calculation and interpretation of molecular properties associated with the MEP of chemical systems. Future work will be devoted to establish connections between ϵ^Q and molecular properties such as proton affinities and pK_a .

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for structural formulas of the set of 75 organic and inorganic molecules containing H, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, and Ar nuclei (Table S1); kinetic energy (KE), orbital energy (ϵ^Q), electronic (E1) and nuclear (N1) components of $\langle V(r_Q) \rangle$, and electronic (E2) and nuclear (N2) components of the MEP for all the 512 nuclei, using four combinations of electronic and nuclear basis sets (Tables S2-S5); correlation parameters of $\langle V(r_Q) \rangle$ vs MEP and $\frac{\epsilon^Q}{Z_Q}$ vs MEP grouped by the type of nucleus (Table S6).

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