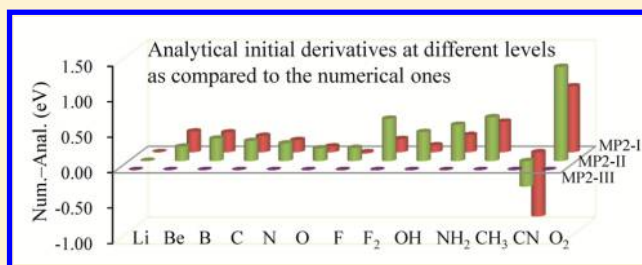


Integration Approach at the Second-Order Perturbation Theory: Applications to Ionization Potential and Electron Affinity Calculations

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ABSTRACT: An integration approach is developed to calculate ionization potentials (IPs), and electron affinities (EAs), which is an extension of the D- Δ MBPT(2) method [A. Beste et al., *J. Chem. Phys.* **2013**, 138, 074101]. The latter is an extension of the single-point method of Cohen et al. [A. J. Cohen et al., *J. Chem. Theory Comput.* **2009**, 5, 786] from the perspective of fractional charges. While relaxation effects were included only at the Hartree–Fock (HF) level in the previous methods, such effects are fully taken into account in the present method up to the second-order Møller–Plesset (MP2) level. This is made possible by deriving the full MP2 energy gradient, with respect to the orbital occupation numbers, which is solved through the coupled-perturbed HF (CP-HF) equations.



I. INTRODUCTION

Ionization potential (IP) and electron affinity (EA) are essential molecular properties of fundamental importance.^{1–4} Many useful concepts, such as electronegativity,⁵ chemical potential,⁶ hardness, and softness,⁷ as well as electrophilicity and nucleophilicity,⁸ etc., are defined on top of IP and EA.

Vertical IP and EA, for the fixed atomic positions at the corresponding N_0 -electron system, are defined as

$$\text{IP} = E(N_0 - 1) - E(N_0) \quad (1)$$

$$\text{EA} = E(N_0) - E(N_0 + 1) \quad (2)$$

where $E(N_0)$ is the ground state energy of the N_0 -electron system with N_0 being an integer, and $E(N_0 \mp 1)$ corresponds to the ground state energy of the $(N_0 \mp 1)$ -electron systems after an electron is removed from or added to the frontier orbitals (i.e., the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO)) of the N_0 -electron system. These equations involve two separate calculations, which can be carried out either at the Hartree–Fock (HF) level or at the post-HF level through, e.g., Møller–Plesset (MP) perturbation theory, etc. and are generally referred to as the Δ methods, such as ΔHF ^{9,10} or ΔMP ,^{11,12} respectively. One of the disadvantages of the Δ methods is that the energy difference (e.g., IP or EA) is typically much smaller than the total energies of the initial and final states, i.e., a small number computed from the subtraction of two large numbers. Hence, there is potentially a precision problem, in particular, when the system size is large.

The precision problem can be avoided in the direct (D) methods (see, e.g., refs 13–28), where IPs and EAs are

computed directly without explicitly involving total energy differences of the initial and final states. The simplest and once frequently used D method is the HF method, under Koopmans' theorem,¹³ according to which IPs and EAs are given by the negatives of the respective orbital energies for the occupied or unoccupied MOs, respectively, in the N_0 -electron system.²⁹ This approximation corresponds to the frozen orbital approximation, where the effects of electron relaxation during the electron removal and addition are neglected. At the HF level, the effects of electron correlation are also neglected. There are several well-known cases, e.g., N_2 and F_2 ,^{30,31} where Koopmans' theorem fails to predict the correct ordering of states, and the inclusion of correlation effects was found to be crucial.^{32,33}

For decades, many methods have been developed to compute directly IPs and EAs at the correlated level.^{14–28} For example, there are the equation-of-motion coupled cluster (EOM-CC) method,^{18–20} the coupled cluster Green's function (CCGF) method,²¹ the coupled cluster linear response theory (CCLRT),²² the Fock space coupled cluster (FSCC) method,^{23,24} the SAC (symmetry-adapted cluster)/SAC-CI (configuration interaction) method,²⁵ the electron propagator method, etc.^{26–28} These CC-based methods are closely related to each other and are generally computationally nontrivial.

While higher-level methods tend to be expensive, the HF method is known to be deficient without considering correlation effects. Thus, MP2 is often applied as the lowest correlation level in the family of wave function methods.^{34–46}

Received: June 23, 2015

Published: September 9, 2015



Recently, Cohen, Mori-Sánchez, and Yang developed an analytical derivative of MP2 by considering the explicit dependence of correlation energies on the orbital occupation numbers,⁴⁵ leading to an expression that may be related to the MP2 single-particle energy. Their expression can also be obtained from the second-order self-energy in propagator theory,²⁸ which corresponds to the lowest level Green's function approach.²⁹ More recently, Beste, Vázquez-Mayagoitia, and Ortiz proposed the D-ΔMBPT(2) method for IP and EA calculations.⁴⁶ They extended the work of Cohen et al.,⁴⁵ by further considering the explicit dependence of orbital energies on the occupation number,⁴⁷ yielding some higher-order terms that are not present in Cohen's expression. However, the expression of Beste et al. is still incomplete,⁴⁶ because the orbital relaxation effects beyond HF are neglected. In analogous to the D-ΔHF method,⁴⁸ they employed a numeric integration technique of the energy derivative in the D-ΔMBPT(2) method. Here, we will further extend the work of Beste et al.,⁴⁶ by considering the full MP2 energy gradient, with respect to the orbital occupation numbers. This is realized by solving the coupled-perturbed HF (CP-HF) equations.

The remainder of this paper is organized as follows. In Section II, we briefly discuss the integration approach to obtain energy differences such as IPs, and EAs, where one-point and two-point equations are employed. We then derive the full MP2 energy derivatives, with respect to the orbital occupation numbers, compared to the formalisms of Cohen et al.⁴⁵ and Beste et al.⁴⁶ Computation details are summarized in Section III, while test calculations are presented in Section IV for some selective atoms and molecules. Finally, we give some concluding remarks in Section V.

II. THEORY

A. The Integration Approach. The integration approach and its significance, as well as its connection to other methods, have been discussed in depth by Beste et al.^{46,48} Here, we only recapitulate it briefly.

The integration approach introduces a coupling parameter λ that defines a pathway to connect two different states of the system. The energy difference between the final state ($\lambda = 1$) and the initial state ($\lambda = 0$) is then calculated as an integral of the derivative of energy, with respect to parameter λ :

$$\Delta E = E(1) - E(0) = \int_0^1 \frac{dE(\lambda)}{d\lambda} d\lambda \quad (3)$$

Since the energy derivative, $((dE(\lambda))/d\lambda)$, is on the same order of magnitude as the energy difference (ΔE) itself, the precision problem is, therefore, avoided.

In terms of standard perturbation theory,²⁹ one can always expand the energy as a polynomial function of λ :

$$E(\lambda) = \sum E^{(k)} \lambda^k = E^{(0)} + E^{(1)} \lambda + E^{(2)} \lambda^2 + E^{(3)} \lambda^3 + \dots \quad (4)$$

such that the derivative is given by

$$\frac{dE(\lambda)}{d\lambda} = E^{(1)} + 2E^{(2)} \lambda + 3E^{(3)} \lambda^2 + \dots \quad (5)$$

If $E(\lambda)$ changes linearly with parameter λ , ΔE is then defined by the initial slope of $E(\lambda)$, i.e., $E^{(1)} = ((dE(\lambda))/d\lambda)|_{\lambda=0}$. Normally, the $E(\lambda)$ curve is not strictly linear; the initial slope only provides an approximation up to the first order,

$$\int_0^1 \frac{dE(\lambda)}{d\lambda} d\lambda \approx \Delta E^{[\rightarrow 1]} = \left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=0} \quad (6)$$

Usually, the quadratic term is the leading term that accounts for the nonlinearity of $E(\lambda)$. Hence, we arrive at a two-point equation for the integral that is exact up to the second order, in terms of the coupling parameter (λ):

$$\int_0^1 \frac{dE(\lambda)}{d\lambda} d\lambda \approx \Delta E^{[\rightarrow 2]} = \frac{1}{2} \left[\left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=0} + \left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=1} \right] \quad (7)$$

Generally, the cubic term makes a relatively small contribution. Note that $\Delta E^{[\rightarrow 2]}$ leads to an error of $1/2 E^{(3)} + \dots$, where contributions from the higher-order terms are exaggerated.

For an accurate and efficient calculation of the integral, the energy derivative, with respect to parameter λ , shall be readily computed accurately and efficiently. For the IP or EA calculations that we are interested in here, an obvious choice to define the integration pathway is to relate parameter λ to the orbital occupation number, n_i^λ , where the electron detachment or attachment occurs at the i -th orbital. Here and in the following discussion, we use the labels p , q , r , s , and t to represent any canonical HF spin orbitals. While the orbital occupation number of p , q , r , and s can be either 0 or 1, but not in between, the orbital occupation number of the t -th orbital fulfills $n_t^\lambda \in [0, 1]$. We also adopt the common labels where i , j , and k stand for the occupied canonical HF spin orbitals, and a , b , and c for the virtual canonical HF spin orbitals. In particular, $t = k$ refers to an IP calculation, while $t = c$ refers to an EA calculation, as will be discussed below.

Let the N_0 -electron system correspond to the initial state, and the $(N_0 \mp 1)$ -electron systems correspond to the final state. For IP calculations, from eq 3, we assume that the electron in the k -th orbital is ionized, and a series of hypothetical fractional charge systems are generated to connect the initial ($n_k^0 = 1$) and final ($n_k^1 = 0$) states. Along this path, only the k -th orbital can be fractionally occupied, while the remaining orbitals keep integer occupations, such that we have

$$\begin{aligned} \lambda &= 1 - n_k^\lambda \\ i \leq N_0 \text{ and } i \neq k: n_i^\lambda &= 1 \\ a > N_0: n_a^\lambda &= 0 \end{aligned} \quad (8)$$

Analogously, a series of hypothetical fractional charge systems are generated in order to carry out an EA calculation, which connect the initial ($n_c^0 = 0$) and final ($n_c^1 = 1$) states, where only the c -th orbital can be fractionally occupied:

$$\begin{aligned} \lambda &= n_c^\lambda \\ a > N_0 \text{ and } a \neq c: n_a^\lambda &= 0 \\ i \leq N_0: n_i^\lambda &= 1 \end{aligned} \quad (9)$$

Hence,

$$\text{IP} = \int_0^1 \frac{dE(\lambda)}{d\lambda} d\lambda = - \int_0^1 \frac{dE(\lambda)}{dn_k^\lambda} d\lambda \quad (10)$$

and

$$EA = - \int_0^1 \frac{dE(\lambda)}{d\lambda} d\lambda = - \int_0^1 \frac{dE(\lambda)}{dn_c^\lambda} d\lambda \quad (11)$$

We are now in a position to explore how energies of the systems are dependent on the occupation numbers.

B. The Hartree–Fock Method with Fractional Charges.

The HF total energy may be formulated as

$$E_{\text{HF}}(\lambda) = \sum_{pq}^{\text{all}} P_{pq}^\lambda \langle p^\lambda | \hat{h} | q^\lambda \rangle + \frac{1}{2} \sum_{pqrs}^{\text{all}} P_{pq}^\lambda P_{rs}^\lambda \langle p^\lambda r^\lambda | q^\lambda s^\lambda \rangle \quad (12)$$

where \hat{h} is a one-electron operator that contains the kinetic operator and an external potential \hat{v}_{ext} usually coming from the nuclei ($\hat{h} = -(1/2)\hat{\nabla}^2 + \hat{v}_{\text{ext}}(\vec{r})$), while $\langle p^\lambda r^\lambda | q^\lambda s^\lambda \rangle = \langle p^\lambda r^\lambda | q^\lambda s^\lambda \rangle - \langle p^\lambda r^\lambda | s^\lambda q^\lambda \rangle$ is an antisymmetrized combination of the regular two-electron repulsion integrals:

$$\langle p^\lambda r^\lambda | q^\lambda s^\lambda \rangle = \iint \phi_p^\lambda(\mathbf{x}_1) \phi_q^\lambda(\mathbf{x}_1) r_{12}^{-1} \phi_r^\lambda(\mathbf{x}_2) \phi_s^\lambda(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \quad (13)$$

where \mathbf{x}_1 and \mathbf{x}_2 are combined spatial and spin coordinates. In these equations, p^λ denotes the p -th canonical HF orbital (ϕ_p^λ) from the self-consistent-field (SCF) calculation, which is dependent on λ at a chosen set of occupation numbers, and P_{pq}^λ is an element of the one-particle density matrix \mathbf{P} , where only the diagonal element can have a nonzero value that corresponds to orbital occupation n_p^λ :

$$P_{pq}^\lambda = \delta_{pq} n_p^\lambda \quad (14)$$

In the usual HF scheme, the occupation numbers assume values of 1 or 0, for occupied and unoccupied orbitals, respectively. Here, they are extended according to eq 8 or eq 9 to allow fractional occupations. Minimization of the HF total energy (eq 12) is achieved by varying one of the spin orbitals while preserving its normalization and orthogonality to the other spin orbitals. This gives the HF equations, which yield the orbital energies as

$$\epsilon_p^\lambda = \langle p^\lambda | \hat{h} | p^\lambda \rangle + \sum_{rs \neq p}^{\text{all}} P_{rs}^\lambda \langle p^\lambda r^\lambda | p^\lambda s^\lambda \rangle \quad (15)$$

On the other hand, one can differentiate the HF total energy (eq 12), with respect to the occupation number n_t^λ , leading to

$$\frac{dE_{\text{HF}}(\lambda)}{dn_t^\lambda} = \langle t^\lambda | \hat{h} | t^\lambda \rangle + \sum_{pq \neq t}^{\text{all}} P_{pq}^\lambda \langle p^\lambda t^\lambda | q^\lambda t^\lambda \rangle \quad (16)$$

In deriving eq 16, we have recognized the fact that the HF energy is stationary, with respect to the orbital changes, as we use the HF canonical orbitals $\{\phi_p^\lambda\}$. Comparison of eq 16 with eq 15 leads to

$$\frac{dE_{\text{HF}}(\lambda)}{dn_t^\lambda} = \epsilon_t^\lambda \quad (17)$$

Hence, IPs and EAs can readily be calculated at the HF level as

$$IP_{\text{HF}} = \int_0^1 (-\epsilon_k^\lambda) d\lambda \quad (18)$$

$$EA_{\text{HF}} = \int_0^1 (-\epsilon_c^\lambda) d\lambda \quad (19)$$

Approximations up to the first order and the second order for IPs are

$$IP_{\text{HF}(0)}^{[\rightarrow 1]} = - \left. \frac{dE_{\text{HF}}(\lambda)}{dn_k^\lambda} \right|_{\lambda=0} = -\epsilon_k^0 = -\langle k^0 | \hat{h} | k^0 \rangle - \sum_{i \neq k}^{\text{occ}} \langle k^0 i^0 | k^0 i^0 \rangle \quad (20)$$

and

$$IP_{\text{HF}}^{[\rightarrow 2]} = - \frac{1}{2} \left[\left. \frac{dE_{\text{HF}}(\lambda)}{dn_k^\lambda} \right|_{\lambda=0} + \left. \frac{dE_{\text{HF}}(\lambda)}{dn_k^\lambda} \right|_{\lambda=1} \right] = - \frac{1}{2} (\epsilon_k^0 + \epsilon_k^1) \quad (21)$$

In eq 21, the SCF calculation must be performed also at the final state for $\lambda = 1$, leading to $IP_{\text{HF}(1)}^{[\rightarrow 1]} = -((dE_{\text{HF}}(\lambda)/dn_k^\lambda)|_{\lambda=1})$, where the original k -th occupied orbital for $\lambda = 0$ has just become unoccupied.

EAs can be calculated similarly as

$$EA_{\text{HF}(0)}^{[\rightarrow 1]} = - \left. \frac{dE_{\text{HF}}(\lambda)}{dn_c^\lambda} \right|_{\lambda=0} = -\epsilon_c^0 = -\langle c^0 | \hat{h} | c^0 \rangle - \sum_i^{\text{occ}} \langle c^0 i^0 | c^0 i^0 \rangle \quad (22)$$

$$EA_{\text{HF}}^{[\rightarrow 2]} = - \frac{1}{2} \left[\left. \frac{dE_{\text{HF}}(\lambda)}{dn_c^\lambda} \right|_{\lambda=0} + \left. \frac{dE_{\text{HF}}(\lambda)}{dn_c^\lambda} \right|_{\lambda=1} \right] = - \frac{1}{2} (\epsilon_c^0 + \epsilon_c^1) \quad (23)$$

whereas, in eq 23, the label c pertains to the neutral system for $\lambda = 0$, which is originally unoccupied, has just become occupied for $\lambda = 1$ when calculating $EA_{\text{HF}(1)}^{[\rightarrow 1]} = -\epsilon_c^1$.

Note that eq 17 is related to Janak's theorem,⁴⁹ where HF may be considered as an approximate density functional, eqs 20 and 22 are related to Koopmans' theorem,¹³ where orbitals are frozen at the N_0 -electron system for $\lambda = 0$. The relaxation effects can be introduced via two-point equations of eqs 21 and 23.

C. The MP2 Method with Fractional Charges. The total energy of MP2 is given by

$$E_{\text{MP2}}(\lambda) = E_{\text{HF}}(\lambda) + E_{c,\text{MP2}}(\lambda) \quad (24)$$

where the last expression for the MP2 correlation energy, generalized to include occupation numbers,^{45,46,50,51} is given as

$$E_{c,\text{MP2}}(\lambda) = \frac{1}{4} \sum_{pqrs}^{\text{all}} n_p^\lambda n_q^\lambda (1 - n_r^\lambda) (1 - n_s^\lambda) \frac{|\langle p^\lambda q^\lambda | r^\lambda s^\lambda \rangle|^2}{\epsilon_p^\lambda + \epsilon_q^\lambda - \epsilon_r^\lambda - \epsilon_s^\lambda} \quad (25)$$

We now need to determine the derivative of the MP2 correlation energy $E_{c,\text{MP2}}(\lambda)$, with respect to the occupation number n_t^λ :

$$\begin{aligned} \frac{dE_{c,\text{MP2}}(\lambda)}{dn_t^\lambda} &= \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial n_t^\lambda} + \sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \epsilon_p^\lambda} \frac{d\epsilon_p^\lambda}{dn_t^\lambda} \\ &+ \sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \phi_p^\lambda} \frac{d\phi_p^\lambda}{dn_t^\lambda} \end{aligned} \quad (26)$$

Equation 15 shows how ϵ_p^λ is dependent explicitly on the occupation numbers of all orbitals other than n_p^λ :

$$\frac{\partial \epsilon_p^\lambda}{\partial n_t^\lambda} = \langle p^\lambda t^\lambda | p^\lambda t^\lambda \rangle \quad (27)$$

The full derivative of orbital energy, with respect to occupation number, is given by

$$\frac{d\varepsilon_p^\lambda}{dn_t^\lambda} = \frac{\partial \varepsilon_p^\lambda}{\partial n_t^\lambda} + \sum_q^{\text{all}} \frac{\partial \varepsilon_p^\lambda}{\partial \phi_q^\lambda} \frac{d\phi_q^\lambda}{dn_t^\lambda} \quad (28)$$

Hence, we can group the full MP2 correlation energy derivative into three terms:

$$\begin{aligned} \frac{dE_{c,\text{MP2}}(\lambda)}{dn_t^\lambda} &= \underbrace{\frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial n_t^\lambda}}_{\text{(I)}} + \underbrace{\sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \varepsilon_p^\lambda} \frac{\partial \varepsilon_p^\lambda}{\partial n_t^\lambda}}_{\text{(II)}} \\ &+ \underbrace{\sum_q^{\text{all}} \left(\sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \varepsilon_p^\lambda} \frac{\partial \varepsilon_p^\lambda}{\partial \phi_q^\lambda} + \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \phi_q^\lambda} \right) \frac{d\phi_q^\lambda}{dn_t^\lambda}}_{\text{(III)}} \end{aligned} \quad (29)$$

Term I accounts for the explicit dependence of $E_{c,\text{MP2}}(\lambda)$ on the occupation numbers, leading to^{45,46}

$$\begin{aligned} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial n_t^\lambda} &= \frac{1}{2} \sum_{prs}^{\text{all}} \frac{n_p^\lambda (1 - n_r^\lambda) (1 - n_s^\lambda) |\langle p^\lambda t^\lambda | r^\lambda s^\lambda \rangle|^2}{\varepsilon_p^\lambda + \varepsilon_t^\lambda - \varepsilon_r^\lambda - \varepsilon_s^\lambda} \\ &- \frac{1}{2} \sum_{pqs}^{\text{all}} \frac{n_p^\lambda n_q^\lambda (1 - n_s^\lambda) |\langle p^\lambda q^\lambda | t^\lambda s^\lambda \rangle|^2}{\varepsilon_p^\lambda + \varepsilon_q^\lambda - \varepsilon_t^\lambda - \varepsilon_s^\lambda} \end{aligned} \quad (30)$$

If contributions from Terms II and III are omitted, and the energy derivative is only calculated at the initial state for $\lambda = 0$, this is practically the prescription given by Cohen et al. as the MP2 single-particle energy:⁴⁵

$$\begin{aligned} \text{IP}_{\text{MP2}(0)}^{I,[-1]} &= - \left. \frac{dE_{\text{MP2}}^I(\lambda)}{dn_k^\lambda} \right|_{\lambda=0} \\ &= -\varepsilon_k^0 - \frac{1}{2} \left[\sum_j^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle k^{0,0} | a^0 b^0 \rangle|^2}{\varepsilon_k^0 + \varepsilon_j^0 - \varepsilon_a^0 - \varepsilon_b^0} \right. \\ &\quad \left. - \sum_{ij}^{\text{occ}} \sum_b^{\text{vir}} \frac{|\langle i^{0,0} | k^{0,0} b^0 \rangle|^2}{\varepsilon_i^0 + \varepsilon_j^0 - \varepsilon_k^0 - \varepsilon_b^0} \right] \end{aligned} \quad (31)$$

$$\begin{aligned} \text{EA}_{\text{MP2}(0)}^{I,[-1]} &= - \left. \frac{dE_{\text{MP2}}^I(\lambda)}{dn_c^\lambda} \right|_{\lambda=0} \\ &= -\varepsilon_c^0 - \frac{1}{2} \left[\sum_j^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle c^{0,0} | a^0 b^0 \rangle|^2}{\varepsilon_c^0 + \varepsilon_j^0 - \varepsilon_a^0 - \varepsilon_b^0} \right. \\ &\quad \left. - \sum_{ij}^{\text{occ}} \sum_b^{\text{vir}} \frac{|\langle i^{0,0} | c^{0,0} b^0 \rangle|^2}{\varepsilon_i^0 + \varepsilon_j^0 - \varepsilon_c^0 - \varepsilon_b^0} \right] \end{aligned} \quad (32)$$

Note that we have added a superscript I in eqs 31 and 32 to show that only Term I has been considered in computing the MP2 correlation energy derivatives. These expressions can also be obtained from the second-order self-energy in propagator theory,²⁸ which corresponds to the lowest level Green's function approach,²⁹ and has also been used to calculate the quasiparticle band gap of solids.^{52,53}

Under the Term I approximation, IPs and EAs can also be evaluated up to the second order by using the two-point equation:

$$\text{IP}_{\text{MP2}}^{I,[-2]} = - \frac{1}{2} \left(\left. \frac{dE_{\text{MP2}}^I(\lambda)}{dn_k^\lambda} \right|_{\lambda=0} + \left. \frac{dE_{\text{MP2}}^I(\lambda)}{dn_k^\lambda} \right|_{\lambda=1} \right) \quad (33)$$

$$\text{EA}_{\text{MP2}}^{I,[-2]} = - \frac{1}{2} \left(\left. \frac{dE_{\text{MP2}}^I(\lambda)}{dn_c^\lambda} \right|_{\lambda=0} + \left. \frac{dE_{\text{MP2}}^I(\lambda)}{dn_c^\lambda} \right|_{\lambda=1} \right) \quad (34)$$

where the energy derivatives also must be calculated at the final state for $\lambda = 1$.

Beste et al. extended the work of Cohen et al.,⁴⁵ by further considering the explicit dependence of orbital energies on the occupation number (i.e., Term II), yielding some higher-order terms (HOT)⁴⁷ that are not present in Cohen's expression:

$$\begin{aligned} \sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \varepsilon_p^\lambda} \frac{\partial \varepsilon_p^\lambda}{\partial n_t^\lambda} &= - \frac{1}{4} \sum_{pqrs}^{\text{all}} n_p^\lambda n_q^\lambda (1 - n_r^\lambda) (1 - n_s^\lambda) \\ &\times \frac{|\langle p^\lambda q^\lambda | r^\lambda s^\lambda \rangle|^2}{(\varepsilon_p^\lambda + \varepsilon_q^\lambda - \varepsilon_r^\lambda - \varepsilon_s^\lambda)^2} \\ &\times [\langle t^\lambda p^\lambda | t^\lambda p^\lambda \rangle + \langle t^\lambda q^\lambda | t^\lambda q^\lambda \rangle - \langle t^\lambda r^\lambda | t^\lambda r^\lambda \rangle - \langle t^\lambda s^\lambda | t^\lambda s^\lambda \rangle] \end{aligned} \quad (35)$$

If the t -th orbital happens to be an occupied orbital, we have, at $\lambda = 0$,

$$\begin{aligned} \sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \varepsilon_p^\lambda} \frac{\partial \varepsilon_p^\lambda}{\partial n_k^\lambda} \bigg|_{\lambda=0} &= - \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle i^{0,0} | a^0 b^0 \rangle|^2}{(\varepsilon_i^0 + \varepsilon_j^0 - \varepsilon_a^0 - \varepsilon_b^0)^2} \\ &\times [\langle k^{0,0} | k^{0,0} \rangle + \langle k^{0,0} | k^{0,0} \rangle - \langle k^{0,0} | c^{0,0} \rangle - \langle k^{0,0} | c^{0,0} \rangle] \end{aligned} \quad (36)$$

If the t -th orbital is an unoccupied orbital, we have, at $\lambda = 0$,

$$\begin{aligned} \sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \varepsilon_p^\lambda} \frac{\partial \varepsilon_p^\lambda}{\partial n_c^\lambda} \bigg|_{\lambda=0} &= - \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{vir}} \frac{|\langle i^{0,0} | a^0 b^0 \rangle|^2}{(\varepsilon_i^0 + \varepsilon_j^0 - \varepsilon_a^0 - \varepsilon_b^0)^2} \\ &\times [\langle c^{0,0} | c^{0,0} \rangle + \langle c^{0,0} | c^{0,0} \rangle - \langle c^{0,0} | c^{0,0} \rangle - \langle c^{0,0} | c^{0,0} \rangle] \end{aligned} \quad (37)$$

Similar expressions can be obtained at $\lambda = 1$. Adding eqs 30 and 35 together gives an approximate MP2 correlation energy derivative, as developed by Beste et al.⁴⁷ Here, we label it, as the Term II approximation, with a superscript II:

$$\frac{dE_{c,\text{MP2}}^{\text{II}}(\lambda)}{dn_t^\lambda} = \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial n_t^\lambda} + \sum_p^{\text{all}} \frac{\partial E_{c,\text{MP2}}(\lambda)}{\partial \varepsilon_p^\lambda} \frac{\partial \varepsilon_p^\lambda}{\partial n_t^\lambda} \quad (38)$$

Hence, $\text{IP}_{\text{MP2}(\lambda)}^{\text{II},[-1]}$, $\text{EA}_{\text{MP2}(\lambda)}^{\text{II},[-1]}$, $\text{IP}_{\text{MP2}}^{\text{II},[-2]}$, and $\text{EA}_{\text{MP2}}^{\text{II},[-2]}$ can be calculated, up to the first order at $\lambda = 0$ or 1, and the second order, respectively, according to eqs 31–34 after updating $((dE_{\text{MP2}}^I(\lambda))/dn_t^\lambda)$ to $((dE_{\text{MP2}}^{\text{II}}(\lambda))/dn_t^\lambda)$.

We now proceed to develop the full MP2 derivative to take into account the contributions from all three terms shown in eq 29 or eq 26.

D. The Full MP2 Derivative, with Respect to Orbital Occupations. The full MP2 correlation energy derivative, with respect to orbital occupations, is realized here by solving the coupled-perturbed (CP) HF equations, where the formalism can be related to the well-established algorithm for MP2 geometry optimization or calculations of other response properties.^{54–58} Thus, Term I can be analogously referred to as the direct part, depending explicitly on orbital occupations, while Terms II and III can be referenced as the indirect part

coming from the orbitals' responses, which are dependent explicitly on orbital occupations.

We assume that the orbital derivatives, with respect to the t -th orbital occupation, can be expanded by the canonical HF orbitals $\{\phi_q^\lambda\}$:

$$\frac{d\phi_p^\lambda}{dn_t^\lambda} = \sum_q^{\text{all}} \phi_q^\lambda U_{pq}^{\lambda, n_t} \quad (39)$$

where U_{pq}^{λ, n_t} is an element in U^{λ, n_t} , which is a rotation matrix that allows for orbital mixing due to the changing of orbital occupations. Since we are using one-point and two-point equations to approximate the integration approach, only the derivatives at $\lambda = 0$ or $\lambda = 1$ are desired. We will then drop the λ -dependence for partial charges and only consider the cases for integer occupations for the time being.

The virtual-occupied (v-o) block $U_{v-o}^{n_t}$ must be determined by solving the CP-HF equations:^{54–58}

$$\mathbf{A}' U_{v-o}^{n_t} = \mathbf{B}_{v-o, t} \quad (40)$$

For a given spin σ (α or β), the matrix elements are defined by

$$A_{p_\sigma q_\sigma, rs}^\sigma = -(\epsilon_r - \epsilon_s) \delta_{p_\sigma} \delta_{q_\sigma} - A_{p_\sigma q_\sigma, rs}^\sigma \quad (41)$$

$$A_{p_\sigma q_\sigma, rs}^\sigma = \langle p_\sigma r || q_\sigma s \rangle + \langle p_\sigma s || q_\sigma r \rangle \quad (42)$$

and

$$B_{p_\sigma q_\sigma, t}^\sigma = \langle p_\sigma t || q_\sigma t \rangle \quad (43)$$

To settle the full U^{n_t} matrix, we need additional blocks, i.e., $U_{o-o}^{n_t}$ from occupied-occupied (o-o) orbitals, and $U_{v-v}^{n_t}$ from virtual-virtual (v-v) orbitals:^{54–58}

$$U_{bc}^{n_t} = \frac{1}{\epsilon_c - \epsilon_b} (\sum_{ia} A_{bc, ai} U_{ai}^{n_t} + B_{bc, t}) \quad (44)$$

$$U_{kj}^{n_t} = \frac{1}{\epsilon_j - \epsilon_k} (\sum_{ia} A_{kj, ai} U_{ai}^{n_t} + B_{kj, t}) \quad (45)$$

The U^{n_t} matrix has the property

$$U_{pq}^{n_t} + U_{qp}^{n_t} = 0 \quad (46)$$

Similarly, the full derivatives of orbital energies can be expressed as

$$\frac{d\epsilon_p}{dn_t} = \sum_{ia} A_{pp, ai} U_{ai}^{n_t} + B_{pp, t} \quad (47)$$

while $B_{pp, t}$ as suggested by eq 47, corresponds to eq 27 for $\partial\epsilon_p/\partial n_t$.

The contributions of the indirect part from Terms II and III can be formulated as

$$\begin{aligned} & \sum_p^{\text{all}} \left(\frac{\partial E_{c, \text{MP2}}(\lambda)}{\partial \epsilon_p^\lambda} \frac{d\epsilon_p^\lambda}{dn_t^\lambda} + \frac{\partial E_{c, \text{MP2}}(\lambda)}{\partial \phi_p^\lambda} \frac{d\phi_p^\lambda}{dn_t^\lambda} \right) \\ &= \sum_{ij} P_{ij}^{(2)} B_{ij, t} + \sum_{ab} P_{ab}^{(2)} B_{ab, t} + 2 \sum_{ia} L_{ai}^{\text{MP2}} U_{ai}^{n_t} \end{aligned} \quad (48)$$

Here, $P_{ij}^{(2)}$ and $P_{ab}^{(2)}$ are the elements of the standard MP2 correction matrix $\mathbf{P}^{(2)}$ to the one-particle density matrix, which correspond to the o-o block and the v-v block, respectively. They are defined as^{54–58}

$$P_{ij}^{(2)} = -\frac{1}{2} \sum_{kab} t_{ik}^{ab} t_{jk}^{ab} \quad (49)$$

and

$$P_{ab}^{(2)} = \frac{1}{2} \sum_{ijc} t_{ij}^{ac} t_{ij}^{bc} \quad (50)$$

where t_{ij}^{ab} is the double substitution amplitude^{54–58}

$$t_{ij}^{ab} = \frac{\langle ij || ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (51)$$

L_{ai}^{MP2} refers to the element of the well-known MP2 Lagrangian \mathbf{L}^{MP2} ,^{59–61}

$$\begin{aligned} L_{ai}^{\text{MP2}} = & -\frac{1}{2} \sum_{jkb} t_{jk}^{ab} \langle jk || ib \rangle + \frac{1}{2} \sum_{jcb} t_{ij}^{cb} \langle aj || cb \rangle \\ & + \sum_{jk} P_{jk}^{(2)} \langle ja || ki \rangle + \sum_{bc} P_{bc}^{(2)} \langle ba || ci \rangle \end{aligned} \quad (52)$$

which is related to the v-o block of $\mathbf{P}^{(2)}$, well-known as the Z-vector method:⁵⁹

$$\mathbf{P}_{v-o}^{(2)} \mathbf{A}' = \mathbf{L}^{\text{MP2}} \quad (53)$$

From eq 40, one has

$$\mathbf{L}^{\text{MP2}} \cdot \mathbf{U}_{v-o}^{n_t} = \mathbf{L}^{\text{MP2}} \mathbf{A}'^{-1} \mathbf{B}_{v-o, t} \quad (54)$$

Noting that $\mathbf{P}_{o-v}^{(2)}$ = transpose($\mathbf{P}_{v-o}^{(2)}$), and using eqs 53 and 54, the last term of eq 48 can be reformulated as

$$2\mathbf{L}^{\text{MP2}} \cdot \mathbf{U}_{v-o}^{n_t} = \mathbf{P}_{v-o}^{(2)} \cdot \mathbf{B}_{v-o, t} + \mathbf{P}_{o-v}^{(2)} \cdot \mathbf{B}_{o-v, t} \quad (55)$$

Finally, terms on the right-hand side (RHS) of eq 48 can be joined together to have

$$\begin{aligned} & \sum_p^{\text{all}} \left(\frac{\partial E_{c, \text{MP2}}(\lambda)}{\partial \epsilon_p^\lambda} \frac{d\epsilon_p^\lambda}{dn_t^\lambda} + \frac{\partial E_{c, \text{MP2}}(\lambda)}{\partial \phi_p^\lambda} \frac{d\phi_p^\lambda}{dn_t^\lambda} \right) = \sum_{pq}^{\text{all}} P_{pq}^{(2)} B_{pq, t} \\ &= \sum_{pq}^{\text{all}} P_{pq}^{(2)} \langle tp || tq \rangle \end{aligned} \quad (56)$$

Thus, instead of directly solving the CP-HF equations for U^{n_t} , we use the Z-vector method to determine the MP2 correction matrix $\mathbf{P}^{(2)}$, which fixes the contributions from Terms II and III for $\lambda = 0$ and $\lambda = 1$. Combining eqs 56 and 30, we arrive at the full MP2 correlation energy derivative, with respect to the orbital occupation number $((dE_{c, \text{MP2}}(\lambda))/dn_t^\lambda)$, which can be used to calculate IPs and EAs with one-point (i.e., $\text{IP}_{\text{MP2}(\lambda)}^{\text{III}[\rightarrow 1]}$, $\text{EA}_{\text{MP2}(\lambda)}^{\text{III}[\rightarrow 1]}$ at $\lambda = 0$ or $\lambda = 1$) and two-point (i.e., $\text{IP}_{\text{MP2}}^{\text{III}[\rightarrow 2]}$, and $\text{EA}_{\text{MP2}}^{\text{III}[\rightarrow 2]}$) equations. The superscript III remains, which is just a reminder of the fact that the MP2 derivative, with respect to the orbital occupation number, has been developed successively to include the explicit dependence of the orbital occupation numbers (I),⁴⁵ orbital eigenvalues (II),⁴⁶ and now orbitals themselves (III).

III. COMPUTATIONAL DETAILS

The previously described formalisms at different levels of approximations have been implemented in the NorthWest Computational Chemistry (NWChem) software package, version 6.1.1.⁶² All calculations were performed in the spin-unrestricted formalisms. No spherical symmetry requirements

Table 1. Comparison of the MP2 Correlation Energy Derivatives, with Respect to the Orbital Occupation Number n_k^λ , for IP Calculations at Different Levels of Approximations^{a,b}

	$\lambda = 0^b$				$\lambda = 1^b$			
	Num ^c	I ^c	II ^c	III ^c	Num ^c	I ^c	II ^c	III ^c
Li	−0.03	−0.03	−0.04	−0.03	−0.04	−0.03	−0.04	−0.04
Be	−0.27	−0.56	−0.47	−0.27	−1.27	−1.28	−1.29	−1.27
B	0.50	0.22	0.18	0.50	−0.85	−0.89	−1.02	−0.85
C	0.84	0.61	0.55	0.84	−1.40	−1.39	−1.55	−1.40
N	1.26	1.09	1.01	1.26	−2.04	−1.98	−2.18	−2.04
O	1.25	1.17	1.07	1.26	−2.76	−2.72	−2.90	−2.76
F	2.11	2.13	1.92	2.11	−3.81	−3.68	−3.94	−3.81
F ₂	4.62	4.43	4.02	4.62	−2.24	−1.25	−2.34	−2.24
OH	1.95	1.85	1.54	1.95	−3.56	−3.44	−3.78	−3.56
NH ₂	1.42	1.18	0.91	1.42	−3.20	−3.11	−3.44	−3.20
CH ₃	1.26	0.83	0.64	1.26	−2.16	−2.23	−2.53	−2.16
CN	1.78	2.69	2.14	1.79	−0.90	−1.13	−2.05	−0.88
O ₂	5.05	4.12	3.72	5.05	−1.08	−0.83	−2.09	−1.08
MAD ^d		0.30	0.41	0.00		0.16	0.30	0.00
MAX ^e		0.93	1.33	0.00		−0.98	1.15	−0.02

^aThe dataset is taken from refs 45, 63, and 64. Values are expressed in units of eV. ^bThe MP2 correlation energy derivative, with respect to the orbital occupation number, is defined by $((dE_{c,MP2}^L(\lambda))/dn_k^\lambda)$, where the orbital index k refers to the HOMO of the N_0 -electron system, which can be partially occupied. The initial state ($\lambda = 0$) corresponds to the N_0 -electron system, where $n_k^0 = 1$, while the final state ($\lambda = 1$) corresponds to the $(N_0 - 1)$ -electron system, where $n_k^1 = 0$, indicating that the k -th orbital has become the LUMO. ^c L indicates the level of approximation. $L = \text{Num}$ stands for a finite difference calculation with $((\Delta E_{c,MP2}^{\text{Num}}(\lambda))/\Delta n_k^\lambda)$, using $\Delta n_k^\lambda = 0.001$. $L = \text{I}$ refers to the approximation where only explicit dependence of the MP2 correlation energy on the occupation number is considered, as in ref 45. $L = \text{II}$ refers to additional consideration of the explicit dependence of the HF eigenvalues on the occupation number, as in ref 46. $L = \text{III}$ is the full MP2 correlation energy derivative developed in the present work. Ideally, one has $\text{Num} = \text{III}$. ^dMean absolute deviation (reference – calculated) from the finite difference results. ^eMaximum absolute deviation (reference – calculated) from the finite difference results.

Table 2. Comparison of the MP2 Correlation Energy Derivatives, with Respect to the Orbital Occupation Number n_c^λ , for EA Calculations at Different Levels of Approximations^{a,b}

	$\lambda = 0^b$				$\lambda = 1^b$			
	Num ^c	I ^c	II ^c	III ^c	Num ^c	I ^c	II ^c	III ^c
Li	−0.52	−0.52	−0.52	−0.52	−0.01	−0.24	−0.15	−0.01
Be	−0.43	−0.48	−0.55	−0.43	0.22	0.03	0.05	0.22
B	−0.97	−0.96	−1.08	−0.96	0.60	0.38	0.36	0.60
C	−1.66	−1.60	−1.78	−1.66	1.14	0.96	0.89	1.14
N	−2.03	−2.00	−2.15	−2.03	0.77	0.82	0.76	0.78
O	−3.19	−3.05	−3.29	−3.19	1.95	2.03	1.81	1.95
F	−4.53	−4.24	−4.60	−4.53	3.18	3.37	2.99	3.19
F ₂	−3.49	−2.68	−3.68	−3.49	4.98	4.83	4.28	4.99
OH	−3.99	−3.78	−4.22	−3.99	2.86	2.78	2.31	2.86
NH ₂	−3.13	−3.04	−3.43	−3.13	1.94	1.67	1.29	1.94
CH ₃	−2.08	−2.05	−2.28	−2.08	0.72	0.40	0.23	0.72
CN	−4.23	−2.89	−3.27	−4.23	2.50	1.80	1.39	2.50
O ₂	−2.77	−2.29	−3.06	−2.77	2.58	2.47	2.03	2.58
MAD ^d		0.28	0.22	0.00		0.21	0.40	0.00
MAX ^e		−1.34	−0.96	−0.01		0.70	1.11	−0.01

^aThe dataset is taken from refs 45, 63, 64. Values are expressed in units of eV. ^bThe MP2 correlation energy derivative, with respect to the orbital occupation number, is defined by $((dE_{c,MP2}^L(\lambda))/dn_c^\lambda)$, where the orbital index c refers to the LUMO of the N_0 -electron system, which can be partially occupied. The initial state ($\lambda = 0$) corresponds to the N_0 -electron system, where $n_c^0 = 0$, while the final state ($\lambda = 1$) corresponds to the $(N_0 + 1)$ -electron system, where $n_c^1 = 1$, indicating that the c -th orbital has become the HOMO. ^c L indicates the level of approximation. $L = \text{Num}$ stands for a finite difference calculation with $((\Delta E_{c,MP2}^{\text{Num}}(\lambda))/\Delta n_c^\lambda)$ using $\Delta n_c^\lambda = 0.001$. $L = \text{I}$ refers to the approximation where only explicit dependence of the MP2 correlation energy on the occupation number is considered as in ref 45. $L = \text{II}$ refers to additional consideration of the explicit dependence of the HF eigenvalues on the occupation number as in ref 46. $L = \text{III}$ is the full MP2 correlation energy derivative developed in the present work. Ideally, one has $\text{Num} = \text{III}$. ^dMean absolute deviation (reference – calculated) from the finite difference results. ^eMaximum absolute deviation (reference – calculated) from the finite difference results.

were imposed on electron densities in atoms. In the numerical calculations of the derivatives $(\Delta E/\Delta n_t)$, Δn_t was chosen as 0.001.⁴⁵ For benchmarking purpose, the variable tol2e in

NWChem,⁶² which determined the integral screening threshold for the evaluation of the energy and related Fock-like matrices, was set very tightly to be 1×10^{-16} . The SCF convergence was



Figure 1. Comparison of the MP2 correlation energy derivatives, with respect to the orbital occupation number n_i^λ at different levels of approximations for $L = \text{I, II, and III}$: (a) initial derivatives corresponding to the HOMO of the N_0 -electron system, (b) final derivatives corresponding to the LUMO of the (N_0-1) -electron system, (c) initial derivatives corresponding to the LUMO of the N_0 -electron system, and (d) final derivatives corresponding to the HOMO of the (N_0+1) -electron system. Here, the differences of numerical and analytical derivatives are displayed, where the numerical derivatives are the references. The energies are given in units of eV, where $t = k$ for IP calculations, and $t = c$ for EA calculations.

satisfied, if the total energy difference of two successive cycles was less than 1×10^{-11} a.u.

We discussed here only the frontier orbitals (i.e., HOMO or LUMO), although our formalisms described above are general and can be also applied to core electrons. All orbitals during SCF were occupied according to the aufbau principle, where only HOMO/LUMO were allowed to be fractionally occupied. Note that the orbital label k or c pertains to the N_0 system for $\lambda = 0$, where $k = \text{HOMO}$ and $c = \text{LUMO}$. For the final state of $\lambda = 1$, the k -th orbital becomes LUMO of the (N_0-1) system when its electron is ionized, while the c -th orbital becomes HOMO of the (N_0+1) system when an electron is added to this orbital.

Numerical testing is performed for a set of atoms (i.e., Li, Be, B, C, N, O, and F), as well as some molecules (i.e., F_2 , OH, NH_2 , CH_3 , CN, and O_2). This dataset was compiled by Cohen, Mori-Sánchez, and Yang in discussing their fractional charge perspective on the band gap problem in density functional theory,⁶³ as well as MP2.⁴⁵ The same set has been used recently to examine the fractional charge behavior of some doubly hybrid functionals.^{64–66} The experimental IP and EA data were generally taken from refs 67 and 68, which were used as reference data for statistics analyses. There are no experimental data available for EAs of Be, N, and F_2 . Hence, the CCSD(T) data from ref 69 were used as references instead. Since we are interested in VIPs, geometries for cations were fixed to be those in the respective neutral molecules,^{69–71} i.e., F_2 (1.4119 Å), OH (0.9697 Å), NH_2 (1.02402 Å, 103.40°), CH_3 (1.079 Å, 120.0°), CN (1.1718 Å), and O_2 (1.2075 Å). For EA calculations, the same experimental geometries of the neutral molecules were also adopted for the anions.

The basis set used in all calculations reported in the present work is cc-pVQZ.^{72,73}

IV. RESULTS AND DISCUSSION

A. MP2 Correlation Energy Derivatives at Different Levels of Approximations. The calculated MP2 correlation energy derivatives, with respect to the orbital occupation

numbers n_i^λ , are collected in Tables 1 and 2. While data in Table 1 correspond to the case of $t = k$, where the electron is to be ionized from the k -th occupied orbital, those in Table 2 correspond to the case of $t = c$, where the electron is to be added to the c -th unoccupied orbital. The derivatives, $((dE_{c,MP2}^L(\lambda))/dn_i^\lambda)$, are evaluated at both $\lambda = 0$ and 1, using different levels of approximations ($L = \text{I, II, and III}$). Here, $L = \text{I}$ refers to the approximation where only an explicit dependence of the MP2 correlation energy on the occupation number is considered, as in ref 45. $L = \text{II}$ refers to additional consideration of the explicit dependence of the HF eigenvalues on the occupation number, as given in ref 46. $L = \text{III}$ is the full MP2 correlation energy derivative developed in the present work. Tables 1 and 2 also summarize the numerical results from finite differences, labeled as $L = \text{Num}$. These numbers serve as references here, although they themselves may suffer from numerical unsteadiness.

From Table 1, it is seen that the MP2 correlation derivatives for electron ionizations are all positive at $\lambda = 0$. They become all negative at $\lambda = 1$. Table 2 shows the opposite trend, where the MP2 correlation derivatives for electron attachment are all negative at $\lambda = 0$, and they become all positive at $\lambda = 1$. These observations show that the correlation effects to the HF orbital energies are dependent on at which point (e.g., initial state for $\lambda = 0$ or final state for $\lambda = 1$) the evaluations are carried out and which orbitals (i.e., occupied or unoccupied) are concerned.

For atomic systems, correlation effects generally become larger along with the increasing electronegatives. There are shell structures when fully/half occupied/unoccupied orbitals are involved. The negative value is generally higher than the positive one in magnitude for a given N_0 -species. For molecular systems, the correlation contributions also become more significant if more electronegative atoms present in the molecule (e.g., $\text{CH}_3 < \text{NH}_2 < \text{OH}$).

As compared to $L = \text{Num}$, $L = \text{I}$ presents a reasonably good approximation with mean absolute deviations (MADs) in the range of 0.16–0.30 eV. The majority of the data from $L = \text{I}$ are smaller in magnitude than those from $L = \text{Num}$, regardless of

how the derivatives are evaluated. The maximum deviation (MAX, reference – calculated) amounts to -1.34 eV occurring at CN when calculating the initial derivative of the electron attachment.

Data in Tables 1 and 2 suggest that $L = \text{II}$ is not necessary a better approximation than $L = \text{I}$. MADs for $L = \text{II}$ range from 0.22 eV to 0.41 eV, which almost consistently underestimates the correlation contribution, compared to $L = \text{I}$, when the derivatives are positive for an occupied orbital (i.e., n_k^0 or n_c^1); however, it overestimates the correlation contribution, compared to $L = \text{I}$, when the derivatives are negative for an unoccupied orbital (i.e., n_k^1 or n_c^0).

Figure 1 depicts the derivative differences, $((\Delta E_{\text{cMP2}}^{\text{Num}}(\lambda))/\Delta n_k^\lambda) - ((dE_{\text{cMP2}}^L(\lambda))/dn_k^\lambda)$, at different levels of approximations using those from $L = \text{Num}$ as references. While Figures 1a and 1b show the cases of $t = k$ for IP calculations using the initial ($\lambda = 0$) and final ($\lambda = 1$) derivatives, respectively, Figures 1c and 1d show the cases of $t = c$ for EA calculations using the initial ($\lambda = 0$) and final ($\lambda = 1$) derivatives, respectively. As is clear, $L = \text{II}$ displays, in many cases, a higher error bar than does $L = \text{I}$. Ideally, one should find that $L = \text{III}$ delivers results identical to those from $L = \text{Num}$. This is indeed the case. As compared to the data from $L = \text{Num}$, $L = \text{III}$ consistently leads to $\text{MAD} = 0.00$ eV, demonstrating that the analytical gradient formalism developed in the present work faithfully takes into account the full MP2 correlation effects upon changing the orbital occupation numbers.

B. Fractional Charge Behavior for Total Energy Versus Electron Number N . From the perspective of fractional charges, it is now well-known that the total energy of a system with a fractional number of electrons $N = N_0 \pm \delta$ with $0 \leq \delta \leq 1$ is a straight line connecting the total energies at the adjacent integers. This was first proved in density functional theory for the Grand Canonical ensemble,⁷⁴ and then was confirmed for the pure state, in consideration of finite systems in the dissociation limit.⁷⁵ Recently, the extension of wave function theories to fractional charges have been explored by Steinmann and Yang.⁷⁶ In recognition of the concave behavior of the HF total energy with respect to the fractional occupations, the straight line behavior is increasingly improved with increasingly sophisticated treatment of correlation effects from MP2 to coupled-cluster singles and doubles (CCSD) to additional perturbative triples, CCSD(T).

For any system with an approximate method, one can check the fractional charge behaviors against the linearity condition.^{45,63,64,76,77} Figure 2 shows, using the O atom as an example, the ground state energy E as a function of the electron number N . The exact straight lines are obtained using the experimental IP (13.61 eV^{65,66}) and EA (1.46 eV^{65,66}) of the O atom. As is clear from Figure 2, MP2 exhibits a much improved linearity, compared to HF, signifying the great importance of the correlation effects.

The inset in Figure 2 shows the deviation from linearity for a given method in another way. It depicts the energy deviations from its own straight line interpolation between adjacent integer values for the O atom (i.e., $\text{O}^+ \leftarrow \text{O} \rightarrow \text{O}^-$). Here, the positive deviations suggest a concave error associated with the HF method, where the largest deviations occur at the respective middle points with the k -th or c -th orbital being half occupied. The errors associated with MP2 for the O atom are obviously smaller than those of HF. While the curves from the HF method are almost quadratic, the MP2 errors change sign at the middle points, having minimum errors at the middle points.

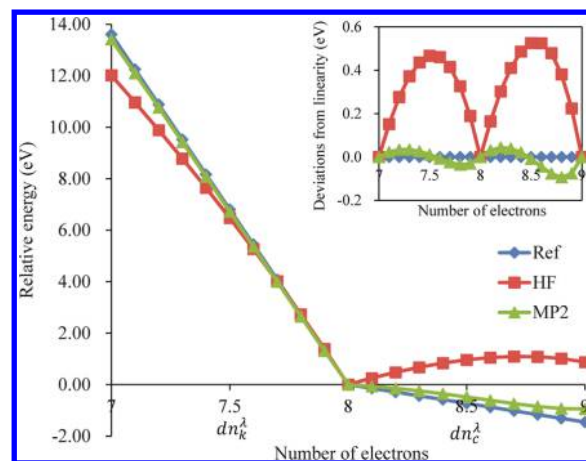


Figure 2. Fractional charge behaviors for the oxygen atom with HF and MP2. The inset depicts the deviations from the corresponding linear interpolations of the methods.

C. Ionization Potential and Electron Affinity Calculated with the HF Method.

Table 3 summarizes the IPs calculated with the HF method using various approximations. Data in the column under the title of $\text{IP}_{\text{HF}(0)}^{[-1]}$ are just the opposite of the orbital energies for the HOMOs of the N_0 -systems, i.e., $\text{IP}_{\text{HF}(0)}^{[-1]} = -\epsilon_{\text{HOMO}}^0$. This corresponds to the well-known Koopmans' theorem.¹³ As orbital relaxation effects are not taken into account, $\text{IP}_{\text{HF}(0)}^{[-1]}$ yields numbers that are consistently too high, compared to the data from ΔHF . On the other hand, data in the column under the title of $\text{IP}_{\text{HF}(1)}^{[-1]}$ are just the opposite of the orbital energies for the LUMO of the (N_0-1) -systems, i.e., $\text{IP}_{\text{HF}(1)}^{[-1]} = -\epsilon_{\text{LUMO}}^1$. If orbitals are fixed at the (N_0-1) -system, which underestimates the stability of the N_0 -system, $\text{IP}_{\text{HF}(1)}^{[-1]}$ yields IPs that are consistently too low, compared to the data from ΔHF . The two-point equation of $\text{IP}_{\text{HF}}^{[-2]}$ combines the two opposite effects of $\text{IP}_{\text{HF}(0)}^{[-1]}$ and $\text{IP}_{\text{HF}(1)}^{[-1]}$, showing good agreement with ΔHF . As shown in Table 3, $\text{MAD}_1/\text{MAX}_1$ from $\text{IP}_{\text{HF}}^{[-2]}$ are $0.15/0.31$ eV, which are 1 order of magnitude smaller than those of $\text{IP}_{\text{HF}(0)}^{[-1]}$ and $\text{IP}_{\text{HF}(1)}^{[-1]}$.

Traditionally, Koopmans's theorem is often used to predict VIPs. This benefits from the lack of both relaxation effect and correlation effect, which tend to cancel each other.^{11,33} Thus, as shown in Table 3, ΔHF consistently underestimates IPs, compared to the experimental values, leading to $\text{MAD}_2 = 0.91$ eV with $\text{MAX}_2 = 1.77$ eV, whereas $\text{IP}_{\text{HF}(0)}^{[-1]}$ consistently overestimates IPs, compared to the experimental values, leading to $\text{MAD}_2 = 1.08$ eV with $\text{MAX}_2 = -2.88$ eV. Note that values from $\text{IP}_{\text{HF}(1)}^{[-1]}$ are generally too small, whose MAD_2 and MAX_2 are 1.97 and 4.01 eV, respectively. $\text{IP}_{\text{HF}}^{[-2]}$ seems to provide the smallest MAD and MAX values of 0.80 and 1.48 eV, respectively.

Figure 2 provides the other way, from the perspective of fractional charges, to look into the HF errors for IP predictions. From $N_0 = 8$ to the left, electron flows out of the O atom, corresponds to the ionization process. $\text{IP}_{\text{HF}(0)}^{[-1]}$ yields the initial derivative, which is quite accurate (erroneous by 0.58 eV). It gradually bends downward after the HOMO orbital is half occupied. $\text{IP}_{\text{HF}(1)}^{[-1]}$ yields the final derivative, which is quite poor (erroneous by 3.24 eV). Ideally, the linearity condition demands $\epsilon_{\text{HOMO}}^0 = \epsilon_{\text{LUMO}}^1$. Hence, the difference $\Delta_{\text{straight}}^{\text{IP,HF}} = \text{IP}_{\text{HF}(0)}^{[-1]} - \text{IP}_{\text{HF}(1)}^{[-1]}$ defines, in a way, the divergence from the linearity. Figure 2 indicates that $E_{\text{HF}}(\lambda)$ is more quadratic than linear. Hence, $\text{IP}_{\text{HF}}^{[-2]}$ provides a better way to approximate IPs.

Table 3. Comparison with the Experimental and Δ HF Results for Ionization Potential (IP) and Electron Affinity (EA) Calculations Using the One-Point and Two-Point Equations

	IP Data					EA Data				
	Expt-IP ^a	Δ HF-IP ^b	IP _{HF(0)} ^{[−1]c}	IP _{HF(1)} ^{[−1]d}	IP _{HF} ^{[−2]e}	Expt-EA ^a	Δ HF-EA ^b	EA _{HF(0)} ^{[−1]c}	EA _{HF(1)} ^{[−1]d}	EA _{HF} ^{[−2]e}
Li	5.39	5.34	5.34	5.34	5.34	0.62	−0.17	−0.29	0.26	−0.01
Be	9.32	8.04	8.42	7.78	8.10	−0.36	−0.92	−1.19	−0.57	−0.88
B	8.30	8.04	8.67	7.51	8.09	0.28	−0.43	−1.09	0.53	−0.28
C	11.26	10.80	11.94	9.85	10.90	1.26	0.33	−0.78	1.84	0.53
N	14.54	13.89	15.52	12.52	14.02	−0.22	−2.26	−3.37	−0.46	−1.91
O	13.61	12.02	14.19	10.37	12.28	1.46	−0.88	−2.64	1.73	−0.46
F	17.42	15.65	18.47	13.41	15.94	3.40	0.90	−1.54	4.27	1.36
F ₂	15.70	16.13	18.13	14.36	16.24	0.42	0.03	−2.37	2.78	0.21
OH	13.01	11.36	13.95	9.39	11.67	1.83	−0.59	−2.61	2.36	−0.12
NH ₂	11.14	10.45	12.59	8.79	10.69	0.77	−1.39	−2.89	0.91	−0.99
CH ₃	9.84	8.98	10.47	7.75	9.11	0.08	−1.96	−2.83	−0.43	−1.63
CN	13.60	12.47	14.65	10.96	12.55	3.86	2.83	0.85	5.11	2.98
O ₂	12.30	13.38	15.18	11.77	13.48	−0.08	−1.21	−2.80	0.73	−1.04
MAD_1 ^f			1.58	1.29	0.15			1.37	1.90	0.27
MAX_1 ^g			−2.82	2.24	0.31			2.44	−3.37	0.47
MAD_2 ^h		0.91	1.08	1.97	0.80		1.46	2.75	0.85	1.26
MAX_2 ⁱ		1.77	−2.88	4.01	1.48		2.50	4.94	−3.53	2.04

^aThe dataset is taken from refs 45, 63, and 64. The values are given in units of eV. The experimental data have been taken from refs 67 and 68, except the EAs for Be, N, F₂ and O₂, which are CCSD(T) data from ref 69. ^bIn the Δ HF method, ionization energy is calculated as $IP = E_{HF}(N_0 - 1) - E_{HF}(N_0)$, while electron affinity is calculated as $EA = E_{HF}(N_0) - E_{HF}(N_0 + 1)$. ^cIP or EA is calculated up to the first order, using the relation $-(dE_{HF}(\lambda)/d\eta_i^{\lambda})|_{\lambda=0} = -\epsilon_i^0$, which corresponds to the HOMO energy of the N_0 -electron system for IP or the LUMO energy of the N_0 -electron system for EA. ^dIP or EA is calculated up to the first order using $-(dE_{HF}(\lambda)/d\eta_i^{\lambda})|_{\lambda=1} = -\epsilon_i^1$, which corresponds to the LUMO energy of the $(N_0 - 1)$ -electron system for IP or HOMO energy of the $(N_0 + 1)$ -electron system for EA. ^eIP or EA is calculated up to the second order, using the relation $-(1/2)(\epsilon_i^0 + \epsilon_i^1)$. ^fMean absolute deviation (reference – calculated) from the Δ HF results. ^gMaximum absolute deviation (reference – calculated) from the Δ HF results. ^hMean absolute deviation (reference – calculated) from the experimental results. ⁱMaximum absolute deviation (reference – calculated) from the experimental results.

Table 4. Comparison with the Experimental and Δ MP2 Results for Ionization Potential (IP) Calculations Using the One-Point and Two-Point Equations

	Expt ^a	Δ MP2 ^b	IP _{MP2(0)} ^{[−1]c}	IP _{MP2(1)} ^{[−1]c}	IP _{MP2} ^{[−2]d}	IP _{MP2(0)} ^{[−1]e}	IP _{MP2(1)} ^{[−1]e}	IP _{MP2} ^{[−2]d}	IP _{MP2(0)} ^{[−1]e}	IP _{MP2(1)} ^{[−1]e}	IP _{MP2} ^{[−2]d}
Li	5.39	5.38	5.37	5.38	5.38	5.38	5.38	5.38	5.37	5.38	5.38
Be	9.32	8.88	8.98	9.06	9.02	8.89	9.06	8.98	8.69	9.05	8.87
B	8.30	8.31	8.45	8.40	8.42	8.49	8.52	8.51	8.17	8.35	8.26
C	11.26	11.30	11.34	11.24	11.29	11.39	11.40	11.39	11.10	11.25	11.18
N	14.54	14.63	14.44	14.50	14.47	14.52	14.70	14.61	14.27	14.57	14.42
O	13.61	13.42	13.02	13.09	13.05	13.11	13.27	13.19	12.93	13.13	13.03
F	17.42	17.37	16.34	17.09	16.72	16.55	17.35	16.95	16.36	17.22	16.79
F ₂	15.70	15.44	13.70	15.61	14.65	14.11	16.70	15.40	13.51	16.59	15.05
OH	13.01	13.06	12.10	12.84	12.47	12.42	13.18	12.80	12.00	12.95	12.48
NH ₂	11.14	11.99	11.41	11.90	11.66	11.68	12.23	11.96	11.17	11.98	11.58
CH ₃	9.84	9.76	9.64	9.98	9.81	9.83	10.28	10.05	9.21	9.91	9.56
CN	13.60	12.93	14.54	15.39	14.97	14.83	16.32	15.57	13.67	15.15	14.41
O ₂	12.30	11.79	11.06	12.60	11.83	11.46	13.86	12.66	10.13	12.85	11.49
MAD_1 ^e			0.59	0.39	0.41	0.47	0.64	0.40	0.71	0.42	0.36
MAX_1 ^f			1.74	2.46	2.04	1.90	3.39	2.64	1.93	2.22	1.48
MAD_2 ^g		0.25	0.61	0.35	0.44	0.54	0.63	0.42	0.69	0.38	0.42
MAX_2 ^h		0.85	2.00	1.79	1.37	1.59	2.72	1.97	2.19	1.55	0.81

^aThe dataset is taken from refs 45, 63, and 64. The values are given in units of eV. The experimental data are taken from refs 67 and 68. ^bIn the Δ MP2 method, ionization energy is calculated as $IP = E_{MP2}(N_0 - 1) - E_{MP2}(N_0)$. ^cIP is calculated up to the first order using $-(dE_{MP2}^L(\lambda)/d\eta_k^{\lambda})$ at $\lambda = 0$ or $\lambda = 1$ under different levels of approximations ($L = I$, as in ref 45; $L = II$, as in ref 46; and $L = III$, as developed in the present work). ^dIP is calculated up to the second order, using $-(1/2)[(dE_{MP2}^L(\lambda)/d\eta_k^{\lambda})|_{\lambda=0} + (dE_{MP2}^L(\lambda)/d\eta_k^{\lambda})|_{\lambda=1}]$. ^eMean absolute deviation from the Δ MP2 results. ^fMaximum absolute deviation from the Δ MP2 results. ^gMean absolute deviation from the experimental results. ^hMaximum absolute deviation from the experimental results.

Table 3 also summarizes the EAs calculated with the HF method using various approximations. Data in the column

under the title of $EA_{HF(0)}^{[−1]}$ are just the opposite of the orbital energies for the LUMOs of the N_0 -systems, i.e., $EA_{HF(0)}^{[−1]} =$

$-\epsilon_{\text{LUMO}}^0$, corresponding to the Koopmans' theorem,^{13,29} while data in the column under the title of $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$ are just the opposite of the orbital energies for the HOMO of the (N_0+1) -systems, i.e., $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]} = -\epsilon_{\text{HOMO}}^1$. Ideally, the linearity condition demands $\epsilon_{\text{LUMO}}^0 = \epsilon_{\text{HOMO}}^1$. Hence, the difference $\Delta_{\text{straight}}^{\text{EA,HF}} = \text{EA}_{\text{HF}(0)}^{[\rightarrow 1]} - \text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$ may also be used as a way to quantify the divergence from linearity.

Table 3 shows the statistics data. $\text{EA}_{\text{HF}(0)}^{[\rightarrow 1]}$ gives data that are too small or even negative, because orbitals are fixed in the N_0 -system while evaluating the total energy of the (N_0+1) -system. As compared to ΔHF , $\text{EA}_{\text{HF}(0)}^{[\rightarrow 1]}$ leads to MAD_1 and MAX_1 values of 1.37 and 2.44 eV, respectively. On the other hand, $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$ overestimates EAs, because orbitals are fixed in the (N_0+1) -system while evaluating the total energy of the N_0 -system. As compared to ΔHF , $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$ leads to MAD_1 and MAX_1 values of 1.90 and -3.37 eV, respectively. Because of the opposite errors of $\text{EA}_{\text{HF}(2)}^{[\rightarrow 1]}$ and $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$, the two-point equation is a good approximation to ΔHF , yielding MAD_1 and MAX_1 values of 0.27 and 0.47 eV, respectively. Note that ΔHF is known to be a poor approximation, because of the lack of correlation effects, which is particularly important in stabilizing the anion systems. As compared to the experimental data, ΔHF underestimates EAs (MAD = 1.46 eV). $\text{EA}_{\text{HF}(0)}^{[\rightarrow 1]}$ diverges even more from the experimental data (MAD = 2.75 eV), because of the accumulating effects of both relaxation effects and correlation effects. $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$, on the other hand, is the most satisfactory method at the level of HF for EA predictions, having MAD of 0.85 eV. Recall that it is well-established in density functional theory that the HOMO energy of the (N_0+1) -system presents a good approximation of EA of the corresponding N_0 -system.

Figure 2 shows the HF energy curve against fractional charges. From $N_0 = 8$ to the right, the electron flows into the O atom, corresponds to the electron attachment process. The curve is clearly concave, which gives initial derivatives that are too small. In fact, EA predicted by $\text{EA}_{\text{HF}(0)}^{[\rightarrow 1]}$ is negative (-2.64 eV), as opposed to the experimental value of 1.46 eV.^{65,66} The final derivative is usually satisfactory. EA predicted by $\text{EA}_{\text{HF}(1)}^{[\rightarrow 1]}$ is 1.73 eV, in fair agreement with the experimental value.

D. Ionization Potential and Electron Affinity Calculated with the MP2 Method. Table 4 summarizes the IPs calculated with the MP2 method using various approximations. Immediately, one finds that the quality of IP calculations are much improved at all levels of MP2 approximations, compared to those for HF. ΔMP2 yields a MAD value of only 0.25 eV, compared to the experimental values. If the one-point equation is employed, $\text{IP}_{\text{MP2}(1)}^{\text{I},[\rightarrow 1]}$ and $\text{IP}_{\text{MP2}(1)}^{\text{III},[\rightarrow 1]}$ lead to MAD_2/MAX_2 values of 0.35/1.79 eV and 0.38/1.55 eV, respectively. These performances are $\sim 0.2/\sim 1.5$ eV better than those from $\text{IP}_{\text{MP2}(0)}^{\text{I},[\rightarrow 1]}$ and $\text{IP}_{\text{MP2}(0)}^{\text{III},[\rightarrow 1]}$. In the literature,^{28,29,45,52,53} the initial derivative, $\text{IP}_{\text{MP2}(0)}^{\text{I},[\rightarrow 1]}$, is most commonly used. $\text{IP}_{\text{MP2}(0)}^{\text{II},[\rightarrow 1]}$ and $\text{IP}_{\text{MP2}(1)}^{\text{II},[\rightarrow 1]}$ lead to comparable MAD_2 values of ~ 0.5 eV, whereas the MAX_2 value is 1.13 eV smaller for the former than for the latter. If the two-point equation is employed, the quality of the calculations is generally similar to that from the one-point equation. $\text{IP}_{\text{MP2}}^{\text{III},[\rightarrow 2]}$ yields a MAD_2 value of 0.42 eV, whose MAX_2 is reduced to 0.81 eV. Note that if more data points are used in the integration approach, only $L = \text{III}$ can faithfully reproduce the ΔMP2 results, because of its nature of accurate analytical MP2 energy gradient, with respect to the orbital occupation numbers.

In fact, ΔMP2 sets up a reference with which all levels of other MP2 approximations can be compared. With the HF

method, we see from Table 3 that IPs evaluated at $\text{IP}_{\text{HF}(0)}^{[\rightarrow 1]}$ and $\text{IP}_{\text{HF}(1)}^{[\rightarrow 1]}$ are too large and small, respectively, compared to ΔHF . Such trends have been compensated by the opposite contributions of the MP2 correlation energy derivatives for $\lambda = 0$ and $\lambda = 1$ (cf. Table 1), leading to similar performances for $\text{IP}_{\text{MP2}(0)}^{[\rightarrow 1]}$ and $\text{IP}_{\text{MP2}(1)}^{[\rightarrow 1]}$, compared to the ΔMP2 values shown in Table 4. The two-point equation usually leads to a smaller error, compared to the one-point equation.

From the perspective of fractional charges, we compare the calculated $\Delta_{\text{straight}}^{\text{IP,MP2}} = \text{IP}_{\text{MP2}(0)}^{[\rightarrow 1]} - \text{IP}_{\text{MP2}(1)}^{[\rightarrow 1]}$ with $\Delta_{\text{straight}}^{\text{IP,HF}} = \text{IP}_{\text{HF}(0)}^{[\rightarrow 1]} - \text{IP}_{\text{HF}(1)}^{[\rightarrow 1]}$. For a better theory, a smaller $\Delta_{\text{straight}}^{\text{IP}}$ is expected according to the linearity condition. We depict $\Delta_{\text{straight}}^{\text{IP}}$ at different levels of theory in Figure 3a. As demonstrated in the

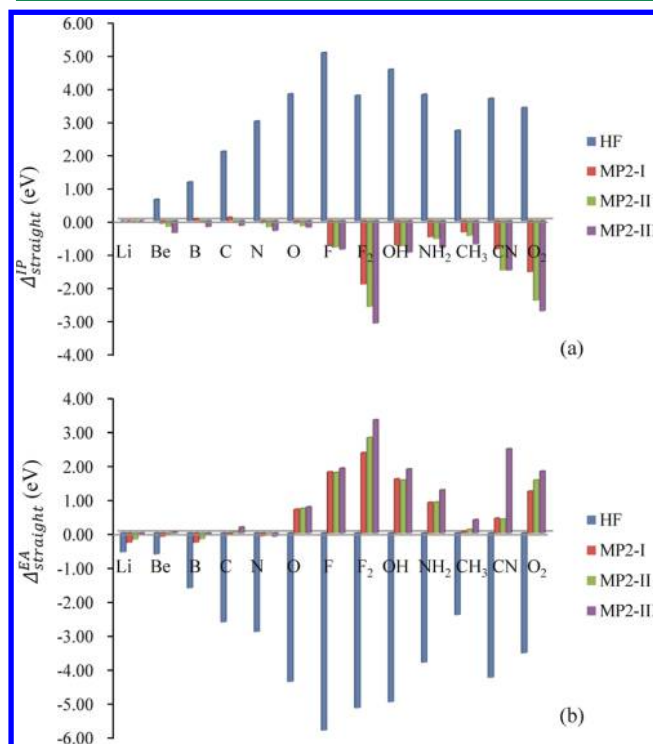


Figure 3. Comparison of the derivative differences, (a) $\Delta_{\text{straight}}^{\text{IP}}$ and (b) $\Delta_{\text{straight}}^{\text{EA}}$ evaluated at the initial state for $\lambda = 0$ and the final state for $\lambda = 1$ with methods of different levels of approximations.

figure, $\Delta_{\text{straight}}^{\text{IP,MP2}}$ is nearly zero for atoms, in agreement with the observation that the MP2 fractional charge curve for total energy is nearly linear (cf. Figure 2 for the O atom). The tendency for increasing $\Delta_{\text{straight}}^{\text{IP}}$ from Li to F at the HF level is largely eliminated at the MP2 level, although sizable errors still exist for the F atom at MP2. MP2 is less satisfactory in molecular species in contrast to its performance in the atomic species. This is particularly the case for F_2 . $\Delta_{\text{straight}}^{\text{IP}}$ amounts to -3.08 eV for MP2 at $L = \text{III}$, which is -1.91 and -2.58 eV, respectively, at $L = \text{I}$ and II . As $L = \text{III}$ is rigorous at the MP2 level, its values reflect the intrinsic deviations of MP2 from the linearity. It is possible that $L = \text{I}$ and II lead to smaller $\Delta_{\text{straight}}^{\text{IP}}$ benefiting from error cancellations.

The EA results calculated with the MP2 method using various approximations are presented in Table 5, which can be compared with the HF results listed in Table 3. While ΔHF is generally faulty for EA predictions, e.g., erroneously predicting an unstable O anion state (see also Figure 2), ΔMP2 corrects such qualitative errors, reducing MAD_2 from 1.46 eV for

Table 5. Comparison with the Experimental and Δ MP2 Results for Electron Affinity (EA) Calculations Using the One-Point and Two-Point Equations

	Expt ^a	Δ MP2 ^b	$EA_{MP2(0)}^{I[-1]}{}^c$	$EA_{MP2(1)}^{I[-1]}{}^c$	$EA_{MP2}^{I[-2]}{}^d$	$EA_{MP2(0)}^{II[-1]}{}^c$	$EA_{MP2(1)}^{II[-1]}{}^c$	$EA_{MP2}^{II[-2]}{}^d$	$EA_{MP2(0)}^{III[-1]}{}^c$	$EA_{MP2(1)}^{III[-1]}{}^c$	$EA_{MP2}^{III[-2]}{}^d$
Li	0.62	0.32	0.23	0.51	0.37	0.23	0.42	0.32	0.22	0.27	0.25
Be	−0.36	−0.75	−0.71	−0.61	−0.66	−0.64	−0.62	−0.63	−0.76	−0.79	−0.78
B	0.28	0.04	−0.13	0.15	0.01	0.00	0.17	0.08	−0.12	−0.07	−0.10
C	1.26	1.09	0.82	0.88	0.85	1.00	0.95	0.98	0.88	0.70	0.79
N	−0.22	−0.87	−1.37	−1.29	−1.33	−1.22	−1.22	−1.22	−1.34	−1.24	−1.29
O	1.46	0.95	0.40	−0.29	0.05	0.65	−0.08	0.28	0.55	−0.22	0.16
F	3.40	3.14	2.70	0.90	1.80	3.06	1.28	2.17	2.99	1.08	2.03
F ₂	0.42	0.04	0.31	−2.05	−0.87	1.31	−1.50	−0.10	1.13	−2.20	−0.54
OH	1.83	1.51	1.17	−0.42	0.37	1.61	0.06	0.83	1.39	−0.50	0.44
NH ₂	0.77	0.40	0.14	−0.76	−0.31	0.54	−0.37	0.08	0.24	−1.03	−0.40
CH ₃	0.08	−0.47	−0.78	−0.83	−0.81	−0.55	−0.66	−0.60	−0.75	−1.15	−0.95
CN	3.86	4.80	3.74	3.31	3.52	4.12	3.72	3.92	5.08	2.60	3.84
O ₂	−0.08	−0.49	−0.51	−1.74	−1.13	0.26	−1.30	−0.52	−0.03	−1.85	−0.94
MAD_1 ^e			0.33	0.99	0.62	0.32	0.74	0.34	0.30	1.08	0.55
MAX_1 ^f			1.06	2.24	1.34	1.27	1.86	0.97	1.09	2.24	1.11
MAD_2 ^g		0.42	0.56	1.20	0.88	0.46	0.96	0.61	0.60	1.36	0.83
MAX_2 ^h		0.94	1.15	2.50	1.60	1.00	2.12	1.23	1.22	2.62	1.39

^aThe dataset is taken from refs 45, 63, and 64. The values are given in units of eV. The experimental data taken from refs 67 and 68, except EAs for Be, N, F₂, and O₂, which are CCSD(T) data from ref 69. ^bIn the Δ MP2 method, electron affinity is calculated as $EA = E_{MP2}(N_0) - E_{MP2}(N_0+1)$. ^cEA is calculated up to the first order, using $-(dE_{MP2}^L(\lambda)/d\eta_c^L)$ at $\lambda = 0$ or $\lambda = 1$ under different levels of approximations ($L = I$ (as in ref 45), II (as in ref 46), and III (developed in the present work)). ^dEA is calculated up to the second order, using $-(1/2)[((dE_{MP2}^L(\lambda)/d\eta_c^L)|_{\lambda=0} + ((dE_{MP2}^L(\lambda)/d\eta_c^L)|_{\lambda=1})]$. ^eMean absolute deviation from the Δ MP2 results. ^fMaximum absolute deviation from the Δ MP2 results. ^gMean absolute deviation from the experimental results. ^hMaximum absolute deviation from the experimental results.

Δ HF to 0.42 eV. $EA_{HF(0)}^{[-1]}$ is practically useless ($MAD_2 = 2.75$ eV), whereas adding correlation contributions removes the major part of errors, reducing MAD_2 to 0.56, 0.46, and 0.60 eV, respectively, for MP2 at the levels of $L = I$, II , and III . $EA_{HF(1)}^{[-1]}$ seems to work reasonably well ($MAD_2 = 0.85$ eV), whereas adding correlation contributions destroys the error cancellation, increasing the MAD_2 values to 1.20, 0.94, and 1.36 eV, respectively. Figure 3b depicts $\Delta_{straight}^{EA}$ at various levels of approximations. The improvement is most evident for atoms, where $\Delta_{straight}^{EA}$ at the MP2 level approaches zero. Deviations from linearity can still be sizable for electronegative atom like F and the molecular species, where higher-order correlations are desired.⁷⁶ As noted in Figure 3, $\Delta_{straight}^{EA}$ could be smaller for $L = I$ and II than for $L = III$. Nonetheless, the derivatives are only exact for $L = III$, which reflect the intrinsic errors associated with the MP2 method.

V. CONCLUDING REMARKS

In the present work, we have derived the formalism to calculate the full MP2 energy derivatives, with respect to the orbital occupation numbers, which is implemented and solved through the CP-HF equations. An integration approach is employed to calculate IPs and EAs, using one-point and two-point equations. The present method is an extension of the D- Δ MBPT(2) method by Beste et al.,⁴⁶ which, in turn, is an extension of the single-point method of Cohen et al.⁴⁵ from the perspective of fractional charges. While relaxation effects were included only at the HF level in the previous methods, such effects are fully taken into account in the present method up to the MP2 level. Numerical tests have been carried out for a selective set of atoms and molecules, which verifies the accuracy and usefulness of the present methodology. Comparison with the HF results signifies the importance to include the correlation effects.

The formalism derived in the present work for calculating the full MP2 derivatives applies only to the integer points for $\lambda = 0$ and $\lambda = 1$. It is important to extend it also to consider the fractional occupations.⁷⁸ Density functional theory has become the leading method in studying the IPs and EAs in materials sciences. Extension of the present work to the conventional functionals (i.e., local density approximations, generalized gradient approximations, hybrid functionals) and the recently developed doubly hybrid functionals is an important future direction.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (Nos. 91027044, 21133004), and the Ministry of Science and Technology (Nos. 2013CB834606, 2011CB808505).

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