

# Chemical Potentials and the One-Electron Hamiltonian of the Second-Order Perturbation Theory from the Functional Derivative Approach

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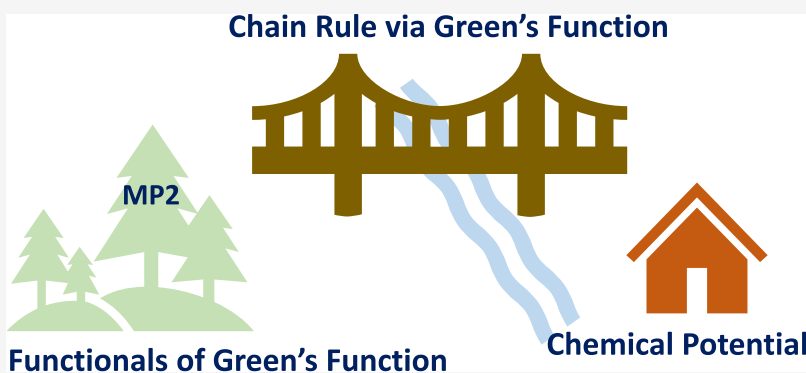
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**ABSTRACT:** We develop a functional derivative approach to calculate the chemical potentials of second-order perturbation theory (MP2). In the functional derivative approach, the correlation part of the MP2 chemical potential, which is the derivative of the MP2 correlation energy with respect to the occupation number of frontier orbitals, is obtained from the chain rule via the noninteracting Green's function. First, the MP2 correlation energy is expressed in terms of the noninteracting Green's function, and its functional derivative to the noninteracting Green's function is the second-order self-energy. Then, the derivative of the noninteracting Green's function to the occupation number is obtained by including the orbital relaxation effect. We show that the MP2 chemical potentials obtained from the functional derivative approach agree with that obtained from the finite difference approach. The one-electron Hamiltonian, defined as the derivative of the MP2 energy with respect to the one particle density matrix, is also derived using the functional derivative approach, which can be used in the self-consistent calculations of MP2 and double-hybrid density functionals. The developed functional derivative approach is promising for calculating the chemical potentials and the one-electron Hamiltonian of approximate functionals and many-body perturbation approaches dependent explicitly on the noninteracting Green's function.

## INTRODUCTION

The chemical potential, defined as the derivative of total energy  $E$  with respect to  $N$ , the total number of electrons at the fixed external potential, is one of the most important concepts for studying fundamental electronic properties in molecules and materials, such as electron transfer and chemical reactivity.<sup>1</sup> The chemical potentials of the electron removal and addition processes are equal to the negative of the ionization potential (IP) and the electron affinity (EA) based on the exact  $E(N)$  linear condition.<sup>2,3</sup> Although these quantities can be measured by photoemission and inverse photoemission spectroscopy, the computational study can provide insights into understanding electronic structures from basic principles. In the past decades, much effort has been devoted to develop quantum chemistry approaches to predict chemical potentials. Kohn–Sham density functional theory<sup>1,4</sup>

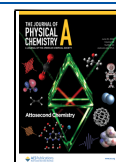
(KS-DFT), as the most popular approach in modern quantum chemistry, has been widely used for molecular and periodic systems.<sup>5–7</sup> In the (generalized) KS-DFT formalism, the orbital energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been shown to be rigorously the chemical potentials for electron removal and electron addition for exchange–correlation energy functionals that are continuous in the KS density matrix.<sup>8</sup> In such cases, which include all

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commonly used exchange–correlation energy functional approximations such as GGA, meta GGA, hybrid, and perturbation-theory-based approximations, the HOMO and LUMO energies are well justified to approximate the negative of the IP and EA because the chemical potentials of the exact functional are the negative of the IP and EA based on the linearity condition for fractional electron numbers.<sup>2,8</sup> For the exact functional, it has been shown to be discontinuous for strongly correlated systems.<sup>9</sup> Therefore, for strongly correlated systems, the chemical potentials are equal to the HOMO and LUMO orbital energies plus the discontinuity contributions. However, DFT has an undesired dependence on the density functional approximations (DFAs), and its accuracy is affected by the intrinsic delocalization error.<sup>10,11</sup> Alternatively, Green's function formalisms such as GW<sup>12–15</sup> and T-matrix<sup>16–18</sup> approximations can be applied for reliable predictions of the chemical potential. In Green's function formalism, the IP and EA are predicted by the quasiparticle energy that directly measures the charged excitation energy. It has been shown that Green's function approaches substantially improve the accuracy of predicting energy levels over the KS-DFT approach for both occupied and unoccupied states, which are the key quantities to calculate IPs, EAs, and core-level binding energies.<sup>16,17,19–25,25–33</sup>

The second-order perturbation theory<sup>34,35</sup> (MP2) has been a long-standing method in the quantum chemistry community. MP2 has been widely employed for predicting many energetic and geometric properties including the electron density, geometry, and energy barrier for both molecular and periodic systems.<sup>36–40</sup> The success of MP2 stems from the improvement over the Hartree–Fock (HF) method and the favorable computational cost compared with those of coupled cluster methods. In addition, the MP2 density matrix is broadly used to generate natural orbitals for the quantum embedding theory.<sup>41,42</sup> However, it is well-known that MP2 fails to describe open-shell systems and transition-metal complexes.<sup>43–45</sup> To address this issue, various methods based on conventional MP2 including spin-component-scaled MP2<sup>43,46,47</sup> (SCS-MP2), orbital-optimized MP2<sup>45,48–50</sup> (OO-MP2), and regularized MP2<sup>51,52</sup> have been developed. The form of the MP2 correlation energy has also been applied in DFT as an approximation to the Görling–Levy second-order perturbation correlation energy,<sup>53</sup> which leads to the double-hybrid functional. In the double-hybrid functional calculations, in addition to the hybridization of the HF exchange, the MP2 correlation energy evaluated with KS orbitals is mixed with a certain portion of the correlation energy.<sup>54–56</sup> A large number of double-hybrid functionals have been developed in the past decades, which significantly outperform conventional DFAs for predicting a broad range of properties including geometries, dissociation energies, thermochemistry, and thermochemical kinetics.<sup>57–77</sup> Recently, the Möller–Plesset adiabatic connection approach that recovers MP2 at small coupling strengths and the correct large-coupling strength expansion has been shown to describe the noncovalent interaction well.<sup>78,79</sup> To calculate the chemical potential, the  $\Delta$ MP2 approach, which calculates the IP and EA by the total energy difference at integer electron numbers, has been used.<sup>80–86</sup> Similar to  $\Delta$ MP2, IPs and EAs can be obtained from the total energy difference of double-hybrid functional calculations at integer electron numbers, which are shown to provide improved accuracy over HF and conventional DFAs.<sup>87</sup> MP2 has also been applied in Green's function formalism. The

second-order Green's function theory (GF2), which corrects the HF orbital energy by the second-order self-energy, has also been applied to predict accurate IPs and EAs HF.<sup>88</sup> Recently, the equation-of-motion MP2 (EOM-MP2) approach has also been developed to calculate IPs and EAs of molecules and solids.<sup>89,90</sup> However, IPs and EAs obtained from these approaches are not the rigorous MP2 chemical potentials, which are the derivatives of the MP2 energy with respect to the particle number.

The extension of MP2 to fractional charge and fraction spin systems has been established by Yang et al.,<sup>91</sup> which allows one to obtain the rigorous MP2 chemical potential. As shown in ref 91, MP2, random phase approximation<sup>88,92</sup> (RPA), particle–particle random phase approximation<sup>93,94</sup> (ppRPA), and a large class of many-body perturbation approaches can be expressed as functionals of the noninteracting Green's function. The fractional formulation of the MP2 correlation energy is achieved by using the ensemble average of the noninteracting Green's function, which is constructed with occupation-scaled orbitals.<sup>91</sup> In fractional MP2 calculations, the fractional charge self-consistent HF calculation is performed first, and then the MP2 correlation energy is evaluated with the HF orbitals obtained for the fractional charge system.<sup>8</sup> With the MP2 correlation energies of the integer and fractional systems, the MP2 chemical potential can be obtained by the finite difference approach, which differentiates the MP2 energy expression with respect to the frontier occupation number with the finite difference. It shows that using the MP2 chemical potential provides better agreement with the experiment IP and EA results compared with using HF orbital energy.<sup>95</sup> By using the fractional formulation of MP2, the analytical approach to calculate the MP2 chemical potential was developed in ref 96. In the analytical approach, the derivative of the MP2 correlation energy to the occupation number is evaluated explicitly, where the orbital relaxation effect is included by solving the coupled-perturbed HF<sup>97–99</sup> equation. It shows that chemical potentials obtained from the analytical approach agree well with those obtained from the finite difference approach.<sup>96</sup> Then, the analytical approach was further applied to calculate the chemical potential of double-hybrid functionals, which shows that the chemical potential of double-hybrid functionals provides smaller errors for predicting IPs and EAs compared with those of HF and conventional DFAs.<sup>87</sup> The analytical approach only needs a system with an integer electron number and thus avoids systems with fractional charge. However, the analytical approach for MP2 cannot be easily extended to other many-body perturbation approaches relying on the noninteracting Green's function.

In the present work, we introduce a functional derivative approach to calculate the MP2 chemical potential. As shown in ref 91, the MP2 correlation energy can be expressed as the integration of the noninteracting Green's function and the second-order self-energy on the real frequency axis, which allows us to calculate the MP2 chemical potential with the chain rule via the noninteracting Green's function. In the functional derivative approach, we first take the functional derivative of the MP2 correlation energy with respect to the noninteracting Green's function, which gives the second-order self-energy. Then, the derivative of the noninteracting Green's function with respect to the occupation number is obtained by solving the CP-HF equation. We show that the MP2 chemical potentials obtained from the functional derivative approach agree with those obtained from the finite difference approach.

As shown in Section 2 in the [Supporting Information](#), for MP2, the functional derivative approach is equivalent to the analytical approach in ref 96. However, the functional derivative approach developed in this work can be easily applied to approximate functionals and many-body perturbation approaches relying on the noninteracting Green's function, such as RPA and ppRPA. Previously, the self-consistent calculation of perturbation theory-based functionals was performed with the optimized effective potential method.<sup>100,101</sup> In this work, we derive the MP2 Hamiltonian using the functional derivative approach, which can be used in the self-consistent calculations of MP2 and double-hybrid functionals in the generalized KS framework with a nonlocal one-electron effective potential.

## METHODS

The traditional MP2 correlation energy<sup>35,102</sup> has been extended to include fractional electrons as<sup>91,95</sup>

$$E_c^{\text{MP2}} = \frac{1}{4} \sum_{pqrs} n_p n_q (1 - n_r)(1 - n_s) \frac{\langle pq||rs \rangle \langle rs||pq \rangle}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \quad (1)$$

where  $n$  is the occupation number,  $\epsilon$  is the orbital energy, and the two-electron integral is defined as  $\langle pq||rs \rangle = \langle pq|rs \rangle - \langle pq|sr \rangle$  with  $\langle pq|rs \rangle = \int d\mathbf{x} d\mathbf{x}' \frac{\psi_p(\mathbf{x})\psi_r(\mathbf{x})\psi_q(\mathbf{x}')\psi_s(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}$ . We use  $i, j, k$ , and  $l$  for occupied orbitals;  $a, b, c$ , and  $d$  for virtual orbitals; and  $p, q, r$ , and  $s$  for general orbitals. Equation 1 is initially used as the finite-temperature extension of MP2 with the fractional occupations from finite temperature excitations<sup>103</sup> and then is derived for fractional systems at zero temperature in ref 91.

As shown in ref 91, the MP2 correlation energy can be expressed as the integration of the noninteracting Green's function and the second-order self-energy on the real frequency axis

$$\begin{aligned} &= \frac{1}{4} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega\eta} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi i} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi i} E_c^{\text{MP2}} \\ &\sum_{pq, rst, uvw} \langle pr||st \rangle \langle uv||qw \rangle G_{su}^0(\omega_1) G_{tw}^0(\omega_2) G_{wr}^0(\omega_1 + \omega_2 - \omega) G_{qp}^0(\omega) \\ &= \frac{1}{4} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega\eta} \text{Tr} \{ \Sigma^{(2)}(\omega) G^0(\omega) \} \end{aligned} \quad (2)$$

where  $\omega$  is the frequency and  $\eta$  is a positive infinitesimal number. In eq 2, the fractional extension of the noninteraction Green's function  $G^0$  in the real space is defined as<sup>91</sup>

$$\begin{aligned} G^0(x_1, x_2, \omega) &= \sum_i \frac{n_i \psi_i(x_1) \psi_i^*(x_2)}{\omega - \epsilon_i - i\eta} \\ &+ \sum_a \frac{(1 - n_a) \psi_a(x_1) \psi_a^*(x_2)}{\omega - \epsilon_a + i\eta} \end{aligned} \quad (3)$$

Note that the fractional orbital is considered to be both the occupied orbital and the virtual orbital. Thus, the fractional orbitals enter both occupied and virtual sets in eq 3.

The second-order self-energy in eq 2 is defined as<sup>88,91,104</sup>

$$\begin{aligned} \Sigma_{pq}^{(2)}(\omega) &= \sum_{rst} \langle pt||rs \rangle \langle rs||qt \rangle \left\{ \frac{(1 - n_r)(1 - n_s)n_t}{\omega - \epsilon_r - \epsilon_s + \epsilon_t + i\eta} \right. \\ &\quad \left. + \frac{n_r n_s (1 - n_t)}{\omega - \epsilon_r - \epsilon_s + \epsilon_t - i\eta} \right\} \end{aligned} \quad (4)$$

which can be separated into two parts

$$\Sigma_{pq}^{+(2)}(\omega) = \sum_{rst} \langle pt||rs \rangle \langle rs||qt \rangle \frac{(1 - n_r)(1 - n_s)n_t}{\omega - \epsilon_r - \epsilon_s + \epsilon_t + i\eta} \quad (5)$$

and

$$\Sigma_{pq}^{-(2)}(\omega) = \sum_{rst} \langle pt||rs \rangle \langle rs||qt \rangle \frac{n_r n_s (1 - n_t)}{\omega - \epsilon_r - \epsilon_s + \epsilon_t - i\eta} \quad (6)$$

As shown in eqs 5 and 6,  $\Sigma^{+(2)}$  has poles below the real frequency axis and  $\Sigma^{-(2)}$  has poles above the real frequency axis. The second-order self-energy in eq 4 is used in GF2 to calculate dissociation energies, band structures, and other properties of molecular and periodic systems.<sup>88,105–109</sup>

With eq 2, the derivative of the MP2 correlation energy to the occupation number can be obtained from the chain rule via the noninteracting Green's function

$$\frac{dE_c^{\text{MP2}}}{dn_p} = \int_{-\infty}^{\infty} d\omega \frac{\delta E_c^{\text{MP2}}}{\delta G^0(\omega)} \frac{dG^0(\omega)}{dn_p} \quad (7)$$

As shown in eq 2, the functional derivative of the MP2 correlation energy to the noninteraction Green's function in eq 7 is simply the second-order self-energy

$$\frac{\delta E_c^{\text{MP2}}}{\delta G_{pq}^0(\omega)} = \frac{1}{2\pi i} \Sigma_{pq}^{(2)}(\omega) \quad (8)$$

Then, with eq 3, the derivative of the noninteracting Green's function with respect to the occupation number consists of three parts

$$\begin{aligned} \frac{dG^0(\omega)}{dn_p} &= \frac{\partial G^0(\omega)}{\partial n_p} + \sum_q \frac{\partial G^0(\omega)}{\partial \epsilon_q} \frac{d\epsilon_q}{dn_p} \\ &+ \left\{ \sum_q \frac{\partial G^0(\omega)}{\partial \psi_q} \frac{d\psi_q}{dn_p} + \text{c. c} \right\} \end{aligned} \quad (9)$$

where the derivative of the orbital energy to the occupation number

$$\frac{d\epsilon_q}{dn_p} = \frac{\partial \epsilon_q}{\partial n_p} + \sum_r \left[ \frac{\partial \epsilon_q}{\partial \psi_r} \frac{d\psi_r}{dn_p} + \text{c. c} \right] \quad (10)$$

and the derivative of the orbital to the occupation number

$$\frac{d\psi_q}{dn_p} = \sum_r \psi_r U_{qr}^p \quad (11)$$

are solved from the CP-HF equation.<sup>97–99</sup> In eq 10, the partial derivative of the orbital energy to the occupation number  $\frac{\partial \epsilon_q}{\partial n_p} = \langle qp||qp \rangle$  is also called the “higher-order term” in ref 82.

Then, we evaluate the three parts in eq 9 separately. The first part in eq 9 is the explicit dependence of the noninteracting Green's function on the orbital occupation number

$$\frac{\partial G^0(x_1, x_2, \omega)}{\partial n_p} = -\frac{\psi_p(x_1)\psi_p^*(x_2)}{\omega - \epsilon_p + i\eta} + \frac{\psi_p(x_1)\psi_p^*(x_2)}{\omega - \epsilon_p - i\eta} \quad (12)$$

The second part in eq 9 is the dependence of the noninteracting Green's function on the orbital energy

$$\frac{\partial G^0(x_1, x_2, \omega)}{\partial \epsilon_p} = \frac{(1 - n_p)\psi_p(x_1)\psi_p^*(x_2)}{(\omega - \epsilon_p + i\eta)^2} + \frac{n_p\psi_p(x_1)\psi_p^*(x_2)}{(\omega - \epsilon_p - i\eta)^2} \quad (13)$$

The third part in eq 9 is the dependence of the noninteracting Green's function on the orbital

$$\frac{\partial G^0(x_1, x_2, \omega)}{\partial \psi_p(x_3)} = \frac{(1 - n_p)\delta(x_1 - x_3)\psi_p^*(x_2)}{\omega - \epsilon_p + i\eta} + \frac{n_p\delta(x_1 - x_3)\psi_p^*(x_2)}{\omega - \epsilon_p - i\eta} \quad (14)$$

$$\frac{\partial G^0(x_1, x_2, \omega)}{\partial \psi_p^*(x_3)} = \frac{(1 - n_q)\psi_p(x_1)\delta(x_2 - x_3)}{\omega - \epsilon_p + i\eta} + \frac{n_q\psi_p(x_1)\delta(x_2 - x_3)}{\omega - \epsilon_p - i\eta} \quad (15)$$

With eqs 12–14, the integral in eq 7 can be performed on the complex plane by using the residue theorem with the contour closing on either the upper half or the lower half plane. Then, the resulting derivative of the MP2 correlation energy with respect to the occupation number consists of the following three parts.

Using eq 12, the first part is

$$I = \Sigma_{pp}^{(2)}(\epsilon_p) = \Sigma_{pp}^{+(2)}(\epsilon_p) + \Sigma_{pp}^{-(2)}(\epsilon_p) \quad (16)$$

which is simply the diagonal element of the second-order self-energy, as shown in refs 91 and 95.

Using eq 13, the second part is

$$II = \sum_q \left[ n_q \frac{d\Sigma_{qq}^{+(2)}(\omega)}{d\omega} \right]_{\omega=\epsilon_q} + (1 - n_q) \left[ \frac{d\Sigma_{qq}^{-(2)}(\omega)}{d\omega} \right]_{\omega=\epsilon_q} \frac{d\epsilon_q}{dn_p} \quad (17)$$

where the diagonal element of the first-order derivative of the second-order self-energy to the frequency is

$$\frac{d\Sigma_{pp}^{+(2)}(\omega)}{d\omega} = -\sum_{rst} \langle pt||rs \rangle \langle rs||pt \rangle \frac{(1 - n_r)(1 - n_s)n_t}{(\omega - \epsilon_r - \epsilon_s + \epsilon_t + i\eta)^2} \quad (18)$$

and

$$\frac{d\Sigma_{pp}^{-(2)}(\omega)}{d\omega} = -\sum_{rst} \langle pt||rs \rangle \langle rs||pt \rangle \frac{n_r n_s (1 - n_t)}{(\omega - \epsilon_r - \epsilon_s + \epsilon_t - i\eta)^2} \quad (19)$$

Using eq 14, the third part is

$$III = \sum_q \left[ n_q \langle \psi_q \left| \Sigma_q^{+(2)}(\epsilon_q) \right| \frac{d\psi_q}{dn_p} \right] + (1 - n_q) \left[ \langle \psi_q \left| \Sigma_q^{-(2)}(\epsilon_q) \right| \frac{d\psi_q}{dn_p} \right] + c. c. \\ = \sum_q [n_q \sum_r \Sigma_{qr}^{+(2)}(\epsilon_q) U_{rq}^p + (1 - n_q) \sum_r \Sigma_{qr}^{-(2)}(\epsilon_q) U_{rq}^p + c. c.] \quad (20)$$

Combining the above three parts together leads to the full derivative of the MP2 correlation energy to the occupation number

$$\frac{dE_c^{MP2}}{dn_p} = I + II + III \\ = \Sigma_{pp}^{+(2)}(\epsilon_p) + \Sigma_{pp}^{-(2)}(\epsilon_p) + \sum_q n_q \frac{d}{dn_p} \Sigma_{qq}^{+(2)}(\epsilon_q) - \sum_q (1 - n_q) \frac{d}{dn_p} \Sigma_{qq}^{-(2)}(\epsilon_q) \quad (21)$$

Because the derivative of the HF total energy to the occupation number is the HF orbital energy,<sup>8,95</sup> the MP2 chemical potential, which is the derivative of the MP2 total energy to the occupation number, is given by

$$\frac{dE_c^{MP2}}{dn_p} = \epsilon_p^{HF} + \frac{dE_c^{MP2}}{dn_p} \quad (22)$$

Equation 22 gives the IP when  $p$  is the HOMO index and the EA when  $p$  is the LUMO index.

The chain rule used for the MP2 correlation energy in eq 7 can be generalized as

$$\frac{dE_c}{dn_p} = \int_{-\infty}^{\infty} d\omega \frac{\delta E_c}{\delta G^0(\omega)} \frac{dG^0(\omega)}{dn_p} \quad (23)$$

Because the derivative of the noninteracting Green's function to the occupation number in eq 23 is not dependent on the correlation energy, it is possible to apply this functional derivative approach to calculate the chemical potential of other approximate functionals and many-body perturbation approaches relying on the noninteracting Green's function.

Similar to eq 7, the correlation part of the MP2 Hamiltonian can also be derived using the functional derivative approach by taking the derivative of the noninteracting Green's function  $G^0$  to the density matrix  $\rho$

$$H_c^{MP2} = \frac{\delta E_c^{MP2}}{\delta \rho} = \int_{-\infty}^{\infty} d\omega \frac{\delta E_c^{MP2}}{\delta G^0(\omega)} \frac{\delta G^0(\omega)}{\delta \rho} \quad (24)$$

As shown in Section 3 in the Supporting Information, the derivative of the noninteracting Green's function to the density matrix is



$$\begin{aligned} \frac{\delta G(x_1, x_2, \omega)}{\delta \rho(x_3, x_4)} &= g(x_1, x_5, \omega + i\eta) f^{\text{Hxc}}(x_5, x_6, x_4, x_3) \\ &\quad g(x_6, x_7, \omega + i\eta) \bar{\rho}_s(x_7, x_2) \\ &\quad + g(x_1, x_5, \omega - i\eta) f^{\text{Hxc}}(x_5, x_6, x_4, x_3) \\ &\quad g(x_6, x_7, \omega - i\eta) \rho_s(x_7, x_2) \\ &\quad + [-g(x_1, x_5, \omega + i\eta) + g(x_1, x_5, \omega - i\eta)] \\ &\quad \delta(x_3, x_5) \delta(x_2, x_4) \end{aligned} \quad (25)$$

where  $\rho_s$  is the density matrix,  $\bar{\rho}_s = I - \rho_s$  is the density matrix of the virtual space, and  $f^{\text{Hxc}}$  is the Hartree-exchange-correlation (Hxc) kernel defined as the functional derivative of the Hxc potential to the density matrix

$$f_{pq,rs}^{\text{Hxc}} = \frac{\delta v_{pq}^{\text{Hxc}}}{\delta \rho_{sr}} \quad (26)$$

and the function  $g(x_1, x_2, \omega)$  is defined as

$$g(x_1, x_2, \omega) = \sum_p \frac{\psi_p(x_1) \psi_p^*(x_2)}{\omega - \epsilon_p} \quad (27)$$

Then, the resulting expression of the Hamiltonian is

$$\begin{aligned} [H_c^{\text{MP2}}]_{pq} &= \frac{\delta E_c^{\text{MP2}}}{\delta \rho_{pq}} \\ &= \frac{1}{2} \sum_{ijab} \frac{\langle ji || ab \rangle \langle ab || ri \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_r)(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)} f_{rj,qp}^{\text{Hxc}} \\ &\quad + \frac{1}{2} \sum_{ijab} \frac{\langle ba || ij \rangle \langle ij || ra \rangle}{(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_r)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)} f_{rb,qp}^{\text{Hxc}} \\ &\quad + \frac{1}{2} [\Sigma_{pq}^{(2)}(\epsilon_q) + \Sigma_{pq}^{(2)}(\epsilon_p)] \end{aligned} \quad (28)$$

In eq 28, the last term that contains the second-order self-energy is dominant, which is similar to the GF2 Hamiltonian with quasiparticle approximation. Similar to the MP2 correlation energy in eq 1 and the second-order self-energy in eq 4, the MP2 Hamiltonian has a divergence issue for systems with a small or vanished band gap, where further studies are needed in future works.

## COMPUTATIONAL DETAILS

We implemented the functional derivative approach for MP2 chemical potential in the QM4D quantum chemistry package.<sup>110</sup> In calculations of the correlation part of MP2 chemical potentials obtained from the functional derivative approach and the finite difference approach, the cc-pVTZ basis set<sup>111–113</sup> was used for CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O. The cc-pVQZ basis set<sup>111–113</sup> was used for the remaining atomic systems. Geometries of CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O were taken from ref 114. In the finite difference approach, the difference in the electron number was 10<sup>−4</sup>. In the calculations of the IPs and EAs of molecular systems, the cc-pVTZ basis set<sup>111–113</sup> was used. Geometries and experiment values were taken from ref 19. The CCSD(T) results calculated from GAUSSIAN16 A.03 software<sup>115</sup> were also used as a reference. All other calculations were performed with a QM4D. QM4D uses Cartesian basis sets and the resolution of identity<sup>86,116,117</sup> (RI) technique to compute two-electron integrals in calculations for the MP2

chemical potential. All basis sets and corresponding fitting basis sets were taken from the Basis Set Exchange.<sup>118–120</sup>

## RESULTS

**Validation of the Functional Derivative Approach for the MP2 Chemical Potential.** We first examined the correlation part of the MP2 chemical potential obtained from the functional derivative approach at different levels of approximations. The finite difference approach and the finite difference approach with frozen orbitals were used as the reference. In the finite difference approach with frozen orbitals, the MP2 correlation energy of fractional charge systems was evaluated with the HF orbitals of the corresponding integer electron system. The finite difference of the electron number was set to 10<sup>−4</sup> in two finite difference approaches. The mean absolute errors (MAEs) of the derivative of the MP2 correlation energy to the HOMO and the LUMO occupation numbers obtained from the functional derivative approach at different levels of approximations compared with the results obtained from two finite difference approaches are listed in Table 1 and Table 2. The first-level approximation (I) only

**Table 1. MAEs of the Correlation Part of the MP2 Correlation Energy with Respect to the HOMO Occupation Number Obtained from the Functional Derivative Approach at Different Levels Compared with the Finite Difference Approach and the Finite Difference Approach with Frozen Orbitals<sup>a</sup>**

	finite diff	finite diff (frozen)	I	I + II	I + II + III
Be	−0.27	−0.56	−0.56	−0.47	−0.27
B	0.50	0.22	0.22	0.19	0.50
C	0.83	0.60	0.60	0.58	0.83
N	1.25	1.07	1.08	1.05	1.25
O	1.26	1.17	1.17	1.17	1.26
F	2.11	2.12	2.13	2.07	2.11
CH <sub>4</sub>	1.09	0.79	0.79	0.77	1.09
NH <sub>3</sub>	1.93	1.62	1.63	1.56	1.93
H <sub>2</sub> O	2.73	2.57	2.58	2.46	2.73
MAE		0.27	0.26	0.29	0.00

<sup>a</sup>In the finite difference approach with frozen orbitals, the MP2 correlation energy of fractional charge systems was evaluated with the HF orbitals of integer electron systems. In finite difference approaches, the difference of the electron number was 10<sup>−4</sup>. The cc-pVTZ basis set was used for CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O. The cc-pVQZ basis set was used for atomic systems. Geometries of CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O were taken from ref 114. All values are in eV.

considers the explicit dependence of the MP2 correlation energy on the occupation number, which is simply the diagonal element of the second-order self-energy, as shown in eq 16. It shows that the first-level approximation provides an MAE smaller than 0.2 eV for the derivative to the HOMO occupation number and smaller than 0.1 eV for the derivative to the LUMO occupation number, which agrees with the results in ref 96. Because the orbital relaxation effect is ignored in the first-level approximation, the results from the first-level approximation and the finite difference approach with frozen orbitals are very close. At the first-level approximation, the functional derivative approach underestimates the derivative to the HOMO occupation number and overestimates the derivative to the LUMO occupation number. The first-level approximation gives similar results to the orbital energies

**Table 2. MAEs of the Correlation Part of the MP2 Correlation Energy with Respect to the LUMO Occupation Number Obtained from the Functional Derivative Approach at Different Levels Compared with the Finite Difference Approach and the Finite Difference Approach with Frozen Orbitals<sup>a</sup>**

	finite diff	finite diff (frozen)	I	I + II	I + II + III
Be	−0.42	−0.47	−0.48	−0.55	−0.42
B	−0.96	−0.96	−0.96	−1.07	−0.96
C	−1.67	−1.61	−1.61	−1.75	−1.66
N	−2.03	−2.03	−2.00	−2.10	−2.03
O	−3.19	−3.19	−3.05	−3.22	−3.19
F	−4.53	−4.24	−4.25	−4.48	−4.53
CH <sub>4</sub>	−0.59	−0.58	−0.58	−0.64	−0.59
NH <sub>3</sub>	−0.65	−0.61	−0.62	−0.70	−0.65
H <sub>2</sub> O	−0.60	−0.60	−0.55	−0.64	−0.60
MAE		0.07	0.07	0.06	0.00

<sup>a</sup>In the finite difference approach with frozen orbitals, the MP2 correlation energy of fractional charge systems was evaluated with the HF orbitals of integer electron systems. In finite difference approaches, the difference of the electron number was  $10^{-4}$ . The cc-pVTZ basis set was used for CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O. The cc-pVQZ basis set was used for atomic systems. Geometries of CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O were taken from ref 114. All values are in eV.

obtained from diagonalizing the MP2 Hamiltonian defined in eq 28. Then, we examine the second-level approximations (I + II) that further consider the dependence of the MP2 correlation energy on the orbital energy. It shows that the second-level approximation provides similar or slightly larger MAEs compared to those of the first-level approximation. As shown in Table 1, the second-level approximation further underestimates the derivative to the HOMO occupation number by around 0.05 eV. And in Table 2, the second-level approximation gives values that are more negative compared with those of the first-level approximation, which leads to similar MAEs. The results of the second-level approximation in this work agree well with the results that include the dependence on the orbital energy in ref 96. The accurate

derivative to the occupation number is obtained by the third-level approximation (I + II + III). In the third-level approximation, the full derivative of the MP2 correlation energy to the occupation number is obtained by further including the dependence on the orbital. The MAEs of the third-level approximation for calculating the derivative to the HOMO and LUMO occupation numbers are 0.0 eV, which means that the results obtained from the functional derivative approach completely agree with the finite difference approach when the orbital relaxation effect is taken into account.

Therefore, we demonstrate that the functional derivative approach is capable of predicting accurate chemical potentials of MP2, which has a simpler form than the analytical approach in ref 96. The equivalence between the functional derivative approach and the analytical approach in ref 96 for calculating MP2 chemical potentials is shown in Section 2 in the Supporting Information.

**IPs and EAs Obtained from the MP2 Chemical Potentials.** Then, we examine the performance of using the MP2 chemical potential for predicting the IPs and EAs of molecular systems. The MAEs of calculated IPs and EAs obtained from HF, MP2,  $\Delta$ HF,  $\Delta$ MP2, and GF2 compared with CCSD(T) results and experimental results are shown in Tables 3 and 4. MP2 means the MP2 chemical potential obtained from the functional derivative approach. In Table 4 of the EA results, MAEs of all systems and bound systems are shown separately. As shown in the literature,<sup>121,122</sup> the prediction of EAs highly depends on basis sets. To obtain fully converged EA results, augmented basis sets and extrapolation schemes are needed.<sup>121,122</sup> In this work, we focus on a comparison between the functional derivative approach and the analytical approach. Thus, the cc-pVTZ basis set was used.

For the prediction of IPs, using HF orbital energies provides a relatively small MAE of 0.77 eV for the small molecular systems in the test set. Because of the lack of correlation effects,  $\Delta$ HF is known to have a poor description for anion systems.<sup>96</sup> Thus,  $\Delta$ HF has a large MAE of 1.16 eV. By including the correlation effects,  $\Delta$ MP2 provides the smallest

**Table 3. MAEs of the Calculated IPs of Molecular Systems Obtained from HF, MP2,  $\Delta$ HF,  $\Delta$ MP2, and GF2<sup>a</sup>**

	HF	$\Delta$ HF	MP2	$\Delta$ MP2	GF2	CCSD(T)	exp
BeO	10.50	7.72	8.29	10.31	7.78	9.97	10.10
BN	11.15	9.78	13.33	11.70	12.04	11.98	
Cl <sub>2</sub>	12.06	11.10	10.67	11.46	11.00	11.41	11.49
CS <sub>2</sub>	10.13	8.73	9.28	10.67	9.83	9.99	10.09
MgF <sub>2</sub>	15.28	13.45	11.93	14.12	11.61	13.68	13.30
F <sub>2</sub>	18.09	15.35	13.40	17.63	13.58	15.67	15.70
Li <sub>2</sub>	4.95	4.35	5.02	4.93	5.21	5.22	4.73
MgCl <sub>2</sub>	12.23	10.65	11.10	11.89	11.31	11.64	11.80
MgO	8.57	4.89	7.40	8.22	6.65	7.77	8.76
Na <sub>2</sub>	4.52	4.11	4.69	4.71	4.85	4.86	4.89
NaCl	9.57	7.97	8.44	9.14	8.59	9.01	9.80
P <sub>2</sub>	10.08	10.07	10.11	10.69	10.57	10.66	10.62
PN	12.02	10.08	11.58	13.14	12.04	11.80	11.88
SO <sub>2</sub>	13.39	11.39	10.79	13.66	11.33	12.21	12.50
MAE CCSD(T)	0.77	1.16	0.90	0.56	0.72		
MAE exp	0.65	1.24	1.04	0.59	0.97	0.28	

<sup>a</sup>MP2 stands for the MP2 chemical potential obtained from the functional derivative approach. CCSD(T) results obtained from GAUSSIAN16 A.03 software<sup>115</sup> and experiment values were used as references. Geometries and experiment values were taken from ref 19. The cc-pVTZ basis set was used. All values are in eV.

**Table 4. MAEs of the Calculated EAs of Molecular Systems Obtained from HF, MP2,  $\Delta$ HF,  $\Delta$ MP2, and GF2<sup>a</sup>**

	HF	$\Delta$ HF	MP2	$\Delta$ MP2	GF2	CCSD(T)
BeO	1.64	2.01	1.89	1.85	2.17	1.95
BN	2.65	4.26	5.07	2.94	3.92	2.77
Cl <sub>2</sub>	-1.14	-0.11	0.89	0.30	0.68	0.14
CS <sub>2</sub>	-1.43	-0.28	0.31	-0.71	0.36	-0.51
MgF <sub>2</sub>	-0.36	-0.28	-0.04	-0.05	-0.05	-0.05
F <sub>2</sub>	-2.55	-0.18	0.78	-0.44	-0.05	-0.66
Li <sub>2</sub>	-0.17	0.32	0.22	0.11	0.23	0.31
MgCl <sub>2</sub>	-0.43	-0.22	0.27	0.22	0.29	0.15
MgO	1.23	2.79	1.78	-0.08	1.25	1.36
Na <sub>2</sub>	-0.05	0.28	0.31	0.16	0.32	0.34
NaCl	0.47	0.53	0.57	0.57	0.59	0.55
P <sub>2</sub>	-0.65	0.00	0.53	-0.05	0.42	0.02
PN	-1.33	-0.35	-0.14	-1.41	-0.28	-0.65
SO <sub>2</sub>	-0.47	0.55	0.77	0.05	0.58	0.14
MAE	0.60	0.38	0.55	0.26	0.36	
MAE (bound)	0.47	0.41	0.49	0.25	0.31	

<sup>a</sup>MP2 stands for the MP2 chemical potential obtained from the functional derivative approach. CCSD(T) results obtained from GAUSSIAN16 A.03 software<sup>115</sup> were used as the reference. MAEs of all systems and bound systems only are listed separately. Geometries were taken from ref 19. The cc-pVTZ basis set was used. All values are in eV.

MAE of 0.56 eV. The MAE of GF2 for IPs is slightly larger than that of  $\Delta$ MP2, which agrees with the results in ref 86. The IPs predicted by the MP2 chemical potential provide a relatively large MAE of 0.90 eV because of the deviations of MP2 from the linearity condition.<sup>123</sup> As shown in ref 123, the accuracy of using the MP2 chemical potential can be improved by using the two-point formula that averages the derivative to the HOMO occupation number of the *N*-electron system and the derivative to the LUMO occupation number of the (*N* - 1)-electron system.

For the prediction of EAs, using HF orbital energies provides the largest MAE of 0.60 eV for all systems and 0.47 eV for the bound system. In addition, HF incorrectly predicts most bound systems as unbound systems.  $\Delta$ HF provides improvements over HF with smaller MAEs around 0.4 eV. Similar to the prediction of IPs,  $\Delta$ MP2 provides the smallest MAE for predicting EAs and correctly describes bound systems except MgO and P<sub>2</sub>. Compared with that of HF, using the MP2 chemical potential correctly describes bound systems. The EAs obtained from the MP2 chemical potential have larger MAEs compared with those of  $\Delta$ MP2, which is similar to the IP results and can also be improved by using the two-point formula.<sup>123</sup>

## CONCLUSIONS

In summary, we developed a functional derivative approach to calculate the MP2 chemical potential. By expressing the MP2 correlation energy as an integration of the noninteracting Green's function and the second-order self-energy on the real frequency axis, the MP2 chemical potential is obtained from the chain rule via the noninteracting Green's function. First, the functional derivative of the MP2 correlation energy with respect to the noninteracting Green's function leads to second-order self-energy. Then, the derivative of the noninteracting Green's function with respect to the occupation number is obtained by including the orbital relaxation effect. We showed

that the MP2 chemical potential from the functional derivative approach agrees with that from the finite difference approach. Then, the MP2 chemical potential obtained from the functional derivative approach was used to predict the IPs and EAs of the molecular systems. It shows that MP2 chemical potentials outperform HF orbital energies for predicting IPs and provide good estimations for EAs. The MP2 Hamiltonian was also derived using the functional derivative approach, which can be used in self-consistent calculations of MP2 and double-hybrid functionals. The developed functional derivative approach for the MP2 chemical potential can be applied to calculate the chemical potential and the one-electron Hamiltonian of approximate functionals and many-body perturbation approaches relying on the noninteracting Green's function, which expands the applicability of the Green's function formalism.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.4c01574>.

Derivation of the functional derivative approach for the MP2 chemical potential, equivalence of the analytical approach and the functional derivative approach for the MP2 chemical potential, and derivation of the MP2 Hamiltonian using the functional derivative approach (PDF)

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### Notes

The authors declare no competing financial interest.

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