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Second-Order Perturbation Theory with Fractional Charges and Fractional Spins

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Abstract: In this work the behavior of MP2 for fractional occupations is investigated. The consideration of fractional charge behavior gives a simple derivation of an expression for the chemical potential (or the derivative of energy with respect to the number of electrons) of MP2. A generalized optimized effective potential formalism (OEP) has been developed in which the OEP is a nonlocal potential, which can be applied to explicit functionals of the orbitals and eigenvalues and also facilitates the evaluation of the chemical potential. The MP2 derivative improves upon the corresponding Koopmans' theorem in Hartree–Fock theory for the ionization energy and also gives a good estimate of the electron affinity. In strongly correlated systems with degeneracies and fractional spins, MP2 diverges, and another corrected second-order perturbative method ameliorates this failure for the energy but still does not recapture the correct behavior for the energy derivatives that yield the gap. Overall we present a view of wave function based methods and their behavior for fractional charges and spins that offers insight into the application of these methods to challenging chemical problems.

Introduction

Recent work^{1–3} has highlighted exact conditions for the energy of systems with fractional charges and fractional spins. These conditions are massively violated by currently used approximations in density functional theory (DFT). The exact energy for fractional charges is a straight line interpolation between the integer points.⁴ Density functional approximations for the exchange–correlation energy (DFAs) such as LDA, GGA,^{5–7} and conventional hybrid functionals⁸ violate this exact condition and have a convex error for the energy of fractional systems. This led to the concept of many-electron self-interaction^{9–11} and a delocalization error¹ that affects the calculation of many differing types of species and properties. Many of the well-known problems of DFAs can be related to this error for fractional charges such as overestimation of molecular polarizabilities, overestimation of molecular conductance, underestimation of charge-transfer excitation energies, underestimation of hydrogen transfer reaction barriers, and underestimation of the band gap in solids. Hartree–Fock (HF) shows the opposite concave behavior^{11,12} for fractional charges and hence an error toward

localization in larger systems. It has also been shown that the exact energy for fractional spins should be constant and at the same energy as the corresponding integer spin pure states. For example the dissociation limit of the H₂ molecule gives two separated atoms each with half an α electron and half a β electron that should be degenerate in energy with the normal H atom. Again HF and DFAs violate this constancy condition and display massive errors for these fractional spin systems that give rise to a large static correlation error. Furthermore, the combination and extension of both fractional charges and fraction spin conditions to consider any general fractional occupations has recently revealed¹³ a much more stringent condition for the energy functional: it has a flat plane behavior, linear along the fractional charge coordinate and constant along the fractional spin coordinate, with a clear line of discontinuity at integer numbers of electrons. Violation of this condition by approximate functionals is important because it leads to qualitative failures to describe, for example, the gap of strongly correlated systems.

With these perspectives we would like to investigate some wave function methods beyond DFT to see if they violate the same exact conditions, by examining simple systems with

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fractional occupations. This may give insight into the relative performance of DFAs and wave function-based methods in challenging situations that are related to delocalization error and static correlation error.

In this work we focus on second-order Møller-Plesset perturbation theory (MP2). MP2 has developed a long standing reputation in the quantum chemistry community and is still a very widely used method with many applications and active development. It reliably alleviates the lack of correlation in HF to give much improved results for many energetic and geometric properties.

Systems with Fractional Charges and Fractional Spins

We explain here how to carry out DFT calculations with fractional charge and fractional spins. The key feature of DFT calculations is the use of a noninteracting reference system to represent the physical electron density and the noninteracting kinetic energy. The noninteracting reference system can have a local one-electron potential, as in the common Kohn–Sham approach (KS), or a nonlocal one-electron potential, as in the generalized Kohn–Sham approach.

In a usual DFT calculation the specification of the charge and the multiplicity of the system are sufficient to give the number of electrons of each spin and hence the set of occupation numbers for the orbitals, $\{n_i\}$. The lowest set of orbitals of each spin (as determined by the energy of the orbital, $\{\varepsilon_i\}$) are occupied ($n_i = 1$), and the higher energy orbitals are unoccupied $n_a = 0$

$$\varepsilon_i \leq \varepsilon_f : n_i = 1 \quad (1)$$

$$\varepsilon_a > \varepsilon_f : n_a = 0 \quad (2)$$

Systems with fractional charge or fractional spins are not themselves physical systems, but they come from the dissociation limits of physical systems,^{13,14} making these fractional systems critical for analyzing the performance of DFAs.

Fractional charge systems can also come from the grand canonical ensemble at zero temperature,⁴ and so do fractional spin systems.³ However, an ensemble calculation with any DFA would clearly give the total energies satisfying the linearity condition for fractional charge and also the constancy condition for fractional spins, making error only at the integer points, even though the DFAs can have massive delocalization and static correlation errors. Therefore such ensemble calculations are not useful for investigating the origins of errors in DFAs. As a system dissociates, such as H_2^+ , the bonding highest occupied molecular orbital (HOMO) becomes delocalized over two centers, and each center sees only part of the HOMO. In other words, the HOMO of each center appears as half-occupied. This is why calculations with fractional orbital occupations in KS or generalized KS are the relevant and important approach for studying DFAs.

Fractional charges and fractional spins are given in practical calculations by a simple change of the occupation numbers, that not all these occupations have to be either one or zero even at zero temperature. For example if we consider

a hypothetical system with fractional charges, then the only way this can appear is with fractional occupation of one orbital, the frontier orbital. For a $J + \delta$ system with J integer and $0 < \delta < 1$ then

$$\varepsilon_i < \varepsilon_f : n_i = 1 \quad (3)$$

$$\varepsilon_f = \varepsilon_f : n_f = \delta \quad (4)$$

$$\varepsilon_a > \varepsilon_f : n_a = 0 \quad (5)$$

In a system with degeneracy it is also possible to get fractional occupations of orbitals, this time even with integer number of electrons, for example a g -fold degeneracy can give

$$\varepsilon_i < \varepsilon_f : n_i = 1 \quad (6)$$

$$\varepsilon_f = \varepsilon_f : \sum_g n_f^g = 1 \quad (7)$$

$$\varepsilon_a > \varepsilon_f : n_a = 0 \quad (8)$$

the n_f^g do not have to be integer. A simple example of this is a hydrogen atom where the α and β orbitals are degenerate leading to the scenario of fractional spins.

To make this point clear, let us consider a simple fractional charge system, for example a hydrogen atom with half an electron, $\text{H}^{1/2+}$. There are two possible ways to view this system: (1) An ensemble average perspective, that requires two calculations on the hydrogen atom, with zero electrons and with one electron, and then taking the appropriate linear combination of the two; and (2) the fractional occupation perspective, where a hydrogen atom with half an electron is explicitly calculated. For the exact energy functional these two views give identical results. However for DFAs the difference between the two is striking: (1) always gives a reasonable answer, as all methods perform well for H and H^+ , and it is only (2) which reveals the failures of the approximate methods, e.g. a too low energy for $\text{H}^{1/2+}$ with LDA, for example. And even more importantly, it is only (2) which corresponds to the energy of stretched H_2^+ , a real integer system.

Thus, for this fractional hydrogen with half an electron, LDA gives a very bad energy, and a better LDA energy could be obtained by the linear combination of the energies of H and H^+ . However, we are not really interested in the best energy of $\text{H}^{1/2+}$ but only in the one that would be obtained if $\text{H}^{1/2+}$ was found in a real system, such as stretched H_2^+ . Thus, we focus on dissociating real systems and understanding the methods, and here is where the fractional occupation approach is very insightful. The power of the fractional occupation perspective relies on the fact that fractional charges and fractional spins do arise naturally in the limit of dissociation of systems with integer occupations and reveal spectacular failures of many currently used methods. Also, as the exact conditions for the energy functional are known for fractional charges and spins, these failures can be understood and better methods developed.

MP2 with Fractional Occupations

We now extend the MP2 expression for fractional occupations, involving unoccupied orbitals, beyond the previous

results of HF and other DFAs containing only occupied orbitals.¹¹ In canonical MP2 from a HF reference Hamiltonian, the correlation energy is given by

$$E_c^{\text{MP2}} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle ij||ab \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \quad (9)$$

where standard notation is used for the two electron integrals, $\langle ij||ab \rangle = \langle ij|ab \rangle - \langle ij|ba \rangle$ and $\langle ij|ab \rangle = \int \int \varphi_i(\mathbf{x})\varphi_a(\mathbf{x})\varphi_j(\mathbf{x}')\varphi_b(\mathbf{x}')d\mathbf{x}d\mathbf{x}'$, where \mathbf{x} and \mathbf{x}' are combined spatial and spin coordinates. In this equation i and j denote occupied orbitals and a and b denote virtual orbitals. All orbitals are canonical HF orbitals, and ε_p represents HF single particle energies (eigenvalues).

This expression can be generalized to include occupation numbers, n_p , by considering the finite temperature grand-canonical ensemble,¹⁵ also see Casida²⁶

$$E_c^{\text{MP2}} = \frac{1}{4} \sum_{ij}^{\text{all}} \sum_{ab}^{\text{all}} n_i n_j \frac{\langle ij||ab \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} (1 - n_a)(1 - n_b) \quad (10)$$

Note that with the inclusion of occupation numbers the summations now run over all orbitals, and there is no separation into occupied and virtual orbitals.

It is now possible to investigate the behavior of the total MP2 energy expression with fractional occupation of the orbitals in an external potential $v(\mathbf{r})$

$$E_v^{\text{MP2}} = \sum_i^{\text{all}} n_i \langle \varphi_i | -\frac{1}{2} \nabla^2 | \varphi_i \rangle + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \sum_{i \geq j}^{\text{all}} n_i n_j \langle ij||ij \rangle + \frac{1}{4} \sum_{ijab}^{\text{all}} n_i n_j \frac{\langle ij||ab \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} (1 - n_a)(1 - n_b) \quad (11)$$

where the occupation numbers, $0 \leq n_i \leq 1$, sum up to give the total number of electrons, $\sum_i^{\text{all}} n_i = N$, and give the electron density, $\rho(\mathbf{r}) = \sum_i^{\text{all}} n_i \varphi_i^2(\mathbf{r})$. In this case the number of electrons, N , does not have to be an integer.

The original finite temperature grand-canonical ensemble⁴ and in the specific case of MP2¹⁵ would give for fractional charge a linear interpolation of energies between the two nearby integers. This is not very interesting, because it does not tell us how the approximate energy functional will behave in physical systems with integer number of electrons but with fractional charge character.¹ Instead, we extend the functional to fractional charges following what has been done for normal KS or HF functionals.^{11,12} Thus, at fractional charges, we carry out the fractional-charge self-consistent HF calculation, and we add the MP2 correlation energy as a perturbation using the HF orbitals obtained for the same fractional charge. We could also carry out the fully self-consistent optimization including the MP2 correlation energy,^{16,17} but we do not do that.

As in previous studies we consider the behavior of the energy expression as we fractionally add or subtract an electron from a zero-temperature ground-state system, $n_i = 1$ for $i < f$, $n_f = \delta$, $n_a = 0$ for $a > f$, where f denotes a frontier

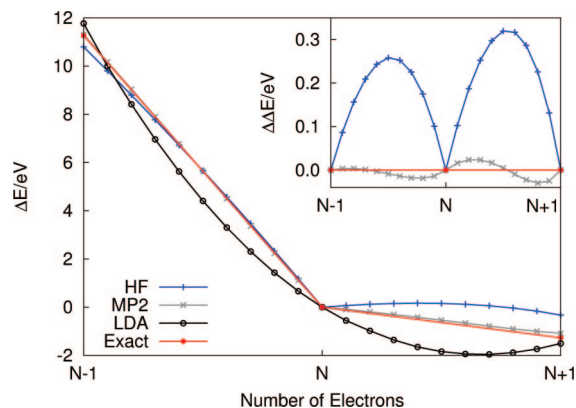


Figure 1. Behavior of the energy of the carbon atom with fractional numbers of electron electrons for HF, MP2, LDA, and exact. The inset shows the deviation of HF and MP2 from their corresponding linear interpolations. All calculations are unrestricted, and no symmetry constraints have been applied.

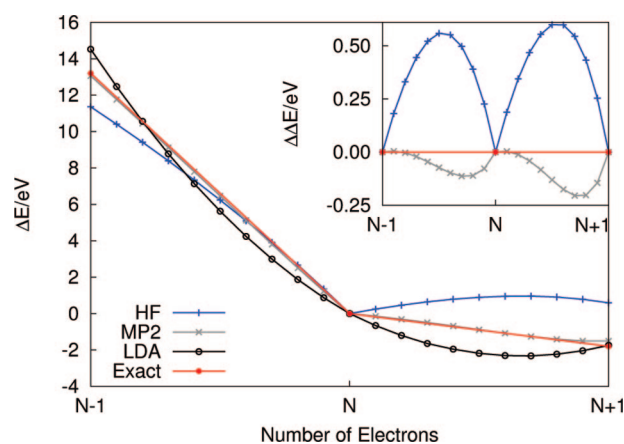


Figure 2. The same as Figure 1 for the OH molecule.

orbital, either the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO).

Figure 1 shows MP2 calculations with fractional numbers of electrons (E vs N curve) for the carbon atom with five to seven electrons. HF and LDA results are also included for comparison. Calculations have been carried out with a cc-pVQZ basis set in a modified version of NWChem.¹⁸ LDA and HF calculations are self-consistent with fixed occupation numbers, and the MP2 energy is given by eq (11) with these fractionally occupied self-consistent HF orbitals. The exact energy for fractional numbers of electrons is a set of straight lines connecting integer points.⁴ For the carbon atom ($N = 6$), the straight line to the left is the ionization energy (experimental value of $I = 11.27$ eV), and the straight line to the right is the negative of the electron affinity (experimental value of $A = 1.27$ eV) as shown in Figure 1. Also shown in the inset is the deviation from the straight line. Another E vs N curve is shown in Figure 2 for the OH molecule which has experimental values of $I = 13.2$ eV and $A = 1.8$ eV.

Previous work¹ has related many important errors of DFAs to the nature of their E vs N curves: concavity giving localization error and convexity giving delocalization error. HF has a large localization error in this respect, and fur-

thermore the integer points are a long way from the exact values of I and A , due to the lack of correlation in HF. MP2 corrects both of these errors of HF for the carbon atom, with a much better prediction of I and A and also importantly a much straighter interpolation between the integers. For OH the MP2 curve is not as straight, and in general the behavior could be checked for any system of interest.

It is clear that HF does not have the correct straight line behavior between the integers, and the concave behavior is best understood as being due to the lack of electron correlation. This is quite different in essence to the behavior of DFAs, as seen for LDA, which have a convex interpolation and delocalization error. For these DFAs as the system size increases to the bulk limit, many-electron self-interaction error decreases causing the E vs N lines to get straighter, however there is a corresponding increase in the delocalization error because the orbitals spread out too much. For HF as the system size increases there is just a growing lack of correlation. Overall, the fact that MP2 and HF do not have this systematic convex behavior means that they will perform differently to DFAs in situations where the delocalization error is important. As MP2 can be closer to the correct straight line behavior and does not in general seem to have an inherent energetic bias for fractional charges, it should have the possibility to have an improved performance in problems related to self-interaction.

Derivatives of the Energy with Respect to N

We now explore the partial derivative of the energy with respect to the total number of electrons, keeping the external potential fixed. This is the chemical potential, and its discontinuity is directly related to the energy gap (band gap in solids). We have recently developed the expressions for evaluating the derivative for calculations with an explicit functional of the electron density or the KS orbitals and eigenvalues.¹⁹ The latter functional can be calculated through the optimized effective potential or through the generalized KS method. Specifically, for a variational method such as LDA, the derivative of the energy with respect to the number of electrons is given by the derivative with respect to the frontier orbital occupation number, $dE_v/dN = (\partial E/\partial n_f)_{v_s} = \epsilon_f$, where v_s is the minimizing local KS potential and ϵ_f is the KS frontier eigenvalue; this result has been obtained from the derivation of ref 19 in combination with the Janak theorem.²⁰ Variational methods that include HF can be treated within a generalized KS equation (where the energy is minimized with respect to the orbitals), and the derivatives of the energy are again given by the frontier eigenvalues as discussed in ref 19.

We now extend the formalism of ref 19 to consider a generalized OEP framework where the energy is minimized with respect to a generalized KS potential $v_s^{NL}(\mathbf{r}, \mathbf{r}')$. In this case the minimizing potential $v_s^{NL,gs}(\mathbf{r}, \mathbf{r}')$ is a nonlocal potential and hence differs from the usual OEP minimizing potential, which is local. This is a simple extension of the potential functional formalism to nonlocal reference potentials for the noninteracting systems.²¹

We consider the potential as the basic variable such that the ground-state energy as a functional of v_s^{NL} and N is given by

$$E_v^{gs} = \min_{v_s^{NL}} E_v[v_s^{NL}, N] = E_v[v_s^{NL,gs}, N] \quad (12)$$

The derivatives with respect to N can be obtained using the chain rule and are simply given by

$$\frac{\partial E_v}{\partial N} = \frac{\partial E_v[v_s^{NL}, N]}{\partial N} \quad (13)$$

$$= \left(\frac{\partial E_v}{\partial N} \right)_{v_s^{NL}} + \int d\mathbf{r} d\mathbf{r}' \frac{\partial E_v}{\partial v_s^{NL}(\mathbf{r}, \mathbf{r}')} \cdot \frac{\partial v_s^{NL}(\mathbf{r}, \mathbf{r}')}{\partial N} \quad (14)$$

At the minimizing $v_s^{NL} = v_s^{NL,gs}$, the second term disappears because the functional is stationary, and we have

$$\frac{\partial E_v}{\partial N} = \left(\frac{\partial E_v}{\partial N} \right)_{v_s^{NL}} \quad (15)$$

Furthermore, at a constant v_s^{NL} , the total number of electron change can only vary the frontier orbital occupation number n_f , and we have

$$\left(\frac{\partial E_v}{\partial N} \right)_{v_s^{NL}} = \left(\frac{\partial E_v}{\partial n_f} \right)_{v_s^{NL}} \quad (16)$$

which is analogous to what we obtained for the usual OEP when the reference potential is local.¹⁹

An example of $E_v[v_s^{NL}, N]$ is the HF energy functional, and its minimizer is just the one-electron nonlocal potential consisting of the Coulomb and exchange operators. The chemical potential for a HF calculation is just given by eq 16. More generally, the generalized OEP formulation of eq 12 allows one to perform DFT calculations for any explicit functional of the orbitals and eigenvalues, such as MP2. This offers an approach to self-consistent DFT, alternative to the local potential OEP.^{16,17}

MP2 is not carried out in a variational fashion but utilizes the minimizing HF potential, $v_s^{NL,HF}$, namely

$$E_v^{\text{MP2}} = E_v^{\text{MP2}}[v_s^{NL,HF}, N] \quad (17)$$

An approximate derivative can be obtained using eq (16)

$$\frac{\partial E_v^{\text{MP2}}}{\partial N} \approx \left(\frac{\partial E[v_s^{NL,HF}, N]}{\partial n_f} \right)_{v_s^{NL,HF}} \quad (18)$$

Applying this expression (eq 18) to the MP2 energy of eq 11 gives an equation for the derivative of the energy with respect to any orbital occupation number

$$\begin{aligned} \left(\frac{\partial E_v^{\text{MP2}}}{\partial n_p} \right)_{v_s^{NL,HF}} &= \langle \varphi_p | -\frac{1}{2} \nabla^2 + v | \varphi_p \rangle + \sum_i 2n_i \langle ip | ip \rangle - \\ &\langle ip | pi \rangle + \frac{1}{2} \left[\sum_{jab} n_j (1 - n_a) (1 - n_b) \frac{\langle pj || ab \rangle^2}{\epsilon_p + \epsilon_j - \epsilon_a - \epsilon_b} - \right. \\ &\left. \sum_{ijb} n_i n_j (1 - n_b) \frac{\langle ij || pb \rangle^2}{\epsilon_i + \epsilon_j - \epsilon_p - \epsilon_b} \right] \quad (19) \end{aligned}$$

When evaluated for a zero temperate ground state, with integer occupations, it gives expressions for the derivatives

Table 1. Comparison, in eV, of $\varepsilon_{\text{HOMO}}$ with $-I$, $\varepsilon_{\text{LUMO}}$ with $-A$, and the $\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$ with $I - A$ for HF and MP2^a

mol	ε_{HF}	$\partial E_{\text{V}}^{\text{MP2}}/\partial n_f$	$I-A$	ε_{HF}	$\partial E_{\text{V}}^{\text{MP2}}/\partial n_f$	I	ε_{HF}	$\partial E_{\text{V}}^{\text{MP2}}/\partial n_f$	A
Li	5.63	5.14	4.8	5.34	5.37	5.4	-0.29	0.23	0.6
Be	9.60	9.69	9.0	8.41	8.98	9.4	-1.19	-0.71	0.4
B	9.76	8.58	8.0	8.67	8.45	8.3	-1.09	-0.13	0.3
C	12.72	10.51	10.00	11.94	11.33	11.27	-0.78	0.82	1.27
N	18.89	15.81	14.46	15.52	14.44	14.53	-3.37	-1.37	0.07
O	16.83	12.77	12.16	14.19	13.17	13.62	-2.64	0.40	1.46
F	20.01	13.71	14.02	18.47	16.41	17.42	-1.54	2.70	3.40
F ₂	20.50	13.39	14.4	18.13	13.70	15.7	-2.37	0.31	1.3
OH	16.56	10.95	11.4	13.95	12.12	13.2	-2.61	1.17	1.8
NH ₂	15.49	11.32	10.6	12.60	11.46	11.4	-2.89	0.14	0.8
CH ₃	13.30	10.42	9.8	10.47	9.64	9.9	-2.83	-0.78	0.1
CN	13.29	10.80	10.2	14.14	14.54	14.0	0.85	3.74	3.8
O ₂	17.98	11.57	11.8	15.18	11.06	12.2	-2.80	-0.51	0.4
MAE	3.84	0.66		0.98	0.56		3.02	0.78	
From finite difference using $\Delta n = 0.001$									
MAE	3.84	0.79		0.98	0.75		3.02	0.70	

^a Calculations are unrestricted with a cc-pVQZ basis set and with no symmetry constraints. MAE the mean absolute error and the MAE for finite difference derivatives of HF and MP2, with a change of the occupation number of 0.001, are also shown.

with respect to frontier occupations and, using eq 18, approximate derivatives of the energy with respect to the number of electrons

$$\left. \frac{\partial E_{\text{V}}^{\text{MP2}}}{\partial N} \right|_{\pm} \approx \left(\frac{\partial E_{\text{V}}^{\text{MP2}}}{\partial n_f} \right)_{v_s^{\text{NL, HF}}} = \langle f | -\frac{1}{2} \nabla^2 + v | f \rangle + \sum_i^{\text{occ}} 2 \langle \langle i f | i f \rangle - \langle i f | f i \rangle \rangle + \frac{1}{2} \left[\sum_j^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{\langle f j | l a b \rangle^2}{\varepsilon_f + \varepsilon_j - \varepsilon_a - \varepsilon_b} - \sum_{ij}^{\text{occ}} \sum_b^{\text{virt}} \frac{\langle i j | l f b \rangle^2}{\varepsilon_i + \varepsilon_j - \varepsilon_f - \varepsilon_b} \right] = \varepsilon_f^{\text{MP2}} \quad (20)$$

For MP2 the single-particle energy of eq 20 does not exactly agree with the full derivative. However the difference is relatively small as can be seen from the comparison with the finite difference calculation of the derivative. For example, for the carbon atom, the finite difference derivative with $\Delta n = 0.001$ gives $\Delta E/\Delta n_{\text{HOMO}} = -11.103$ eV and $\Delta E/\Delta n_{\text{LUMO}} = -0.881$ eV, and eq 20 gives $\partial E/\partial n_{\text{HOMO}} = -11.334$ eV and $\partial E/\partial n_{\text{LUMO}} = -0.824$ eV. The slight difference between the two results is due to the fact that the potential has been fixed, and therefore the second term in eq 14 has been ignored. Fixing the potential at $v_s^{\text{NL, HF}}$ is equivalent to freezing the orbitals and the eigenvalues upon varying the occupation numbers, which is different than just fixing the orbitals. The orbital relaxation can be evaluated using coupled-perturbed HF, but this correction would not be needed if the energy is minimized with respect to the orbitals, as previously done within DFT.^{16,17} Furthermore, the eigenvalues on the bottom of eq 10 can also vary with the occupation number and hence they also contribute. If an expression for the full derivatives of eq 11 with respect to the number of electrons is needed, then these orbital and eigenvalue contributions must be included as dictated by eq 14.

The results in Table 1 compare the HOMO and LUMO single-particle energies from HF and MP2 with the corresponding I and A experimental values of a set of small atoms and molecules. Koopmans' theorem, which equates the HF frontier single-particle energies with $-I$ and $-A$, is improved upon by the second-order MP2 frontier single-particle energies. The MP2 LUMO energy gives a reasonable

approximation to $-A$, whereas the HF LUMO energy seems almost meaningless. The difference between the derivative to the left, I , and the derivative to the right, A , gives the gap which is much improved with MP2 for these small systems. Also the overall mean absolute error calculated with finite difference, which is obviously the same for HF due to its variational nature, shows that the neglected parts of the derivative for MP2 do not lead to any qualitative differences for this set of molecules. The MP2 approximation to I and A and the gap can be obtained at almost no extra cost while doing a normal MP2 calculation.

The expression for the MP2 single-particle energy eq 20 can also be obtained from the second-order self-energy in propagator theory²² and has been used to calculate the quasiparticle band gap of solids.^{23,24} In the present work it is derived in a very simple manner and with a clear connection to the behavior for fractional numbers of electrons. This idea can also be easily extended to other wave function based methods (e.g., coupled cluster) if the method can be generalized to finite temperature to include occupation numbers. Then the behavior for fractional numbers of electrons could be investigated, and the straightness of the E vs N curve will give an indication of the quality of the frontier orbital eigenvalues and more generally on performance of problems related to the delocalization error.

MP2 for Fractional Spins

Next we would like to investigate MP2 for fractional spins to understand its performance on static correlation problems. However, there is very little to explore as the energy for any system with more than one fractional occupation within a degenerate set in eq 10 diverges. This is clearest for the stretched H₂ molecule where the restricted MP2 energy goes to $-\infty$ as shown in Figure 3. Another example is a calculation on the spherical boron atom (with occupation of 1/3 for each of the αp orbitals) where the MP2 energy also diverges. In other words, MP2 fails for systems with strong correlations which is well-known in chemistry as exemplified by the poor performance on transition metal compounds. This failure in degenerate situations can be attempted to be corrected by different techniques, and one of the simplest such methods

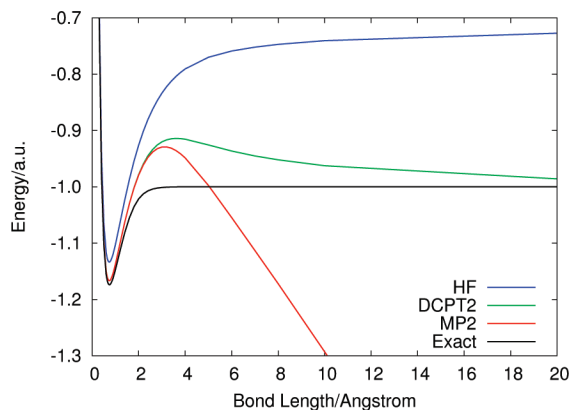


Figure 3. The energy of the H₂ molecule as it is stretched, calculated with a cc-pVQZ basis set with HF, MP2, DCPT2, and exact. It should be noted that the DCPT2 energy goes slightly below -1.0 au at larger distances, e.g. at 10000 Angstrom it is -1.0125 au.

in the literature is the degenerate corrected perturbation theory (DCPT2) of Assfeld et al.²⁵

The DCPT2 correlation energy is given by

$$E_c^{DCPT2} = \frac{1}{8} \sum_{ij}^{occ} \sum_{ab}^{virt} D_{abij} - \sqrt{(D_{abij})^2 + 4\langle ij||ab \rangle^2} \quad (21)$$

where $D_{abij} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$. The inclusion of fractional occupations in an analogous way to MP2 gives

$$E_c^{DCPT2} = \frac{1}{8} \sum_{ijab}^{all} D_{abij} - \sqrt{(D_{abij})^2 + 4n_i n_j \langle ij||ab \rangle^2 (1 - n_a)(1 - n_b)} \quad (22)$$

The total energy of DCPT2 is given by eq 11 replacing the MP2 part with eq 22.

Figure 4 shows the behavior for fractional charge and spin combined for the H atom from zero to two electrons with spin-up occupation $0 \leq n_\alpha \leq 1$ and spin-down occupation $0 \leq n_\beta \leq 1$, as studied previously.¹³ The consideration of this figure and the energy at $[n_\alpha, n_\beta]$ has been critical for understanding the performance of DFT methods and goes beyond the separate consideration of fractional charges, which can be seen along the edges (connecting $[0,0]$ to $[1,0]$ to $[1,1]$ and conversely $[0,0]$ to $[0,1]$ to $[1,1]$), and the pure fractional spins, which can be seen across the middle (connecting $[1,0]$ with $[0,1]$). The problem of a Mott insulator is highlighted by the point at $[1/2, 1/2]$ and its gap from the line $[0,0]$ to $[1/2, 1/2]$ to $[1,1]$.

The exact energy of H $[n_\alpha, n_\beta]$ is plotted in Figure 4a and shows a flat plane behavior with a discontinuous derivative at all points along the constancy line at $N = n_\alpha + n_\beta = 1$. Figure 4b illustrates the behavior of the MP2 energy, which diverges to $-\infty$ except along the pure fractional charge line, seen along the edges of the plot and corresponding to Figure 1. Figure 4c shows the DCPT2 energy of eq 22, which has a very similar behavior to MP2 along the fractional charge line but corrects for the divergence of the MP2 energy expression for fractional spins. There is some slight strange behavior due to the nonanalyticity of the square-root function,

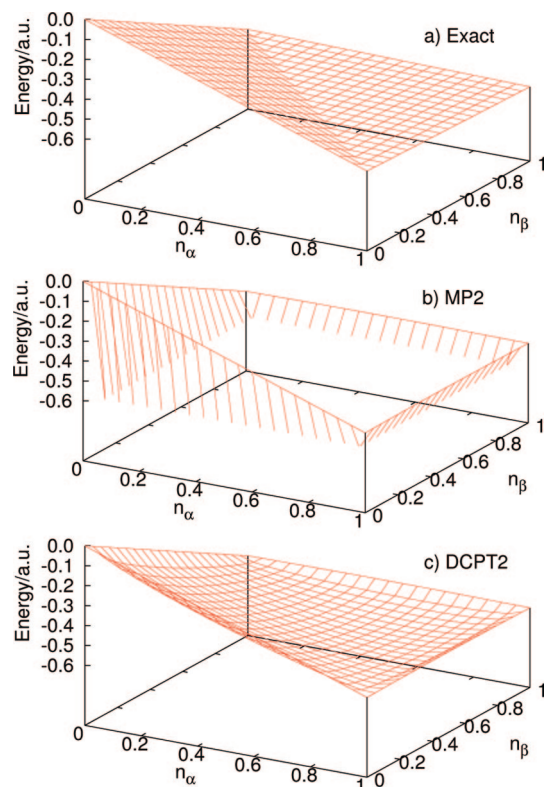


Figure 4. The energy of the hydrogen atom with fractional charges and fractional spins combined for exact, MP2, and DCPT2. All calculations use a cc-pVQZ basis set.

but it only affects points next to the fractional charge line. For the middle point of the plot, an H atom with $n_\alpha = n_\beta = 1/2$ which is the prototype of a strongly correlated system, DCPT2 gives a reasonable energy that exactly corresponds to the dissociation limit of H₂ presented in Figure 3.

It is extremely interesting to see that at the key middle point with $n_\alpha = n_\beta = 1/2$, the slope to the left and the right, $\partial E_v^{DCPT2} / \partial |M_\pm\rangle$, are the same, and therefore there is no discontinuous behavior and a zero gap. This illustrates the possibility for a method to give the energy of a strongly correlated system correctly but still fail to even qualitatively give its gap.

Conclusion

In conclusion, in the spirit of DFT, we have investigated the MP2 method for fractional charges and fractional spins. We find that it gives a reasonable straight line behavior for fractional charges between the integers. A generalized OEP formalism has been developed for nonlocal KS potentials, which can be used to perform DFT calculations for any explicit functional of the orbitals and eigenvalues. It also facilitates the calculation of the chemical potential. Thus, the MP2 single-particle energies can be obtained by differentiating the MP2 energy expression with respect to the frontier occupation numbers at fixed KS potential and give HOMO and LUMO single-particle energies that are in good agreement with experimental $-I$ and $-A$. For fractional spin systems with exact degeneracies MP2 unphysically diverges to give an energy of $-\infty$. Degenerate-corrected perturbation theory alleviates this divergence but still qualitatively fails

for the scenario of combined fractional charge and fractional spins, as it misses the key derivative discontinuity necessary to give the gap.

Overall the understanding of a wave function based method such as MP2 can be enlightened by considering its performance for exact conditions of the energy that can be explored in extremely simple tests.

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References

- (1) Mori-Sánchez, P.; Cohen, A. J.; Yang, W. *Phys. Rev. Lett.* **2008**, *100*, 146401-1–146401-4.
- (2) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *Science* **2008**, *321*, 792–784.
- (3) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *J. Chem. Phys.* **2008**, *129*, 121104.
- (4) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L., Jr. *Phys. Rev. Lett.* **1982**, *49*, 1691–1694.
- (5) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (6) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (7) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (8) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (9) Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 194112-1–194112-8.
- (10) Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2007**, *126*, 104102-1–104102-8.
- (11) Mori-Sánchez, P.; Cohen, A. J.; Yang, W. *J. Chem. Phys.* **2006**, *125*, 201102-1–201102-4.
- (12) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Staroverov, V. N.; Tao, J. *Phys. Rev. A* **2007**, *76*, 040501(R).
- (13) Mori-Sánchez, P.; Cohen, A. J.; Yang, W. *Phys. Rev. Lett.* **2009**, *102*, 066403-1–066403-4.
- (14) Yang, W.; Zhang, Y.; Ayers, P. W. *Phys. Rev. Lett.* **2000**, *84*, 5172–5175.
- (15) Blaizot, J.-P.; Ripka, G. *Quantum Theory of Finite Systems*; The MIT Press: 1986; p 437.
- (16) Mori-Sánchez, P.; Wu, Q.; Yang, W. *J. Chem. Phys.* **2005**, *123*, 062204-1–062204-14.
- (17) Bartlett, R. J.; Lotrich, V. F.; Schweigert, I. V. *J. Chem. Phys.* **2005**, *123*, 062205.
- (18) High Performance Computational Chemistry Group. Pacific Northwest National Laboratory, Richland, Washington 99352, U.S.A., 2002.
- (19) Cohen, A. J.; Mori-Sánchez, P.; Yang, W. *Phys. Rev. B* **2008**, *77*, 115123-1–115123-6.
- (20) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165–7168.
- (21) Yang, W.; Ayers, P. W.; Wu, Q. *Phys. Rev. Lett.* **2004**, *92*, 146404-1–146404-4.
- (22) Linderberg, J.; Öhrn, Y. *Propagators in Quantum Chemistry*; John Wiley & Sons: New York, 1973.
- (23) Pino, R.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 2553–2557.
- (24) Ayala, P. Y.; Kudin, K. N.; Scuseria, G. E. *J. Chem. Phys.* **2001**, *115*, 9698–9707.
- (25) Assfeld, X.; Almlöf, J. E.; Truhlar, D. G. *Chem. Phys. Lett.* **1995**, *241*, 438–444.
- (26) Casida, M. *Phys. Rev. B* **1999**, *59*, 4694–4698.

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