

Proposal for a modified Møller-Plesset perturbation theory

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A modified version of the Møller-Plesset approach for obtaining the correlation energy associated with a Hartree-Fock ground state is proposed. The method is tested in a model of interacting fermions that allows for an exact solution. Using up to third order terms improved results are obtained, even in the limit of loosely bound particles. Tested in molecules as well, the modified method appears to give improved results in symmetric systems.

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I. INTRODUCTION

The study of interacting many-particle systems is seriously constrained by the large dimension of the Hilbert space. Several approximation schemes have been devised over the years, among which the Hartree-Fock (HF) method is one of the oldest and most fruitful, notably in atomic and molecular physics. Because it treats interactions in a mean field way particle correlations are left out, however, a shortcoming that can limit severely the validity of its results. One may improve over HF by treating correlations as a perturbation. In the so-called Møller-Plesset method, a Rayleigh-Schrödinger perturbative expansion that is naturally suggested by the same structure of the HF solution [1–4] is adopted. This formalism reduces the correlation energy to an infinite series in the perturbation, of which only the first few terms need to be computed in practice. This scheme has been used for a long time as a good starting point to study correlation effects in molecular systems. However, this method is useful only if the perturbation series is rapidly convergent, which is not always true [5]. Failures of the Møller-Plesset method have been documented even for small molecules [5–7]. In this paper we present a variation of the Møller-Plesset approach that in some cases appears to give accurate results in low-order perturbation schemes.

Consider the Hamiltonian of a general system of identical particles interacting through a pair potential

$$\mathcal{H} = \sum_i h(i) + \sum_{i,j>i} v(i,j), \quad (1)$$

where $h(i)=h(\mathbf{r}_i)$ is the sum of the one-particle kinetic energy plus external potential energy, and $v(i,j)=v(\mathbf{r}_i,\mathbf{r}_j)$ is the pair-interaction potential. The HF approximation to the ground state of a system of identical fermions leads to a variational wave function Φ in the form of a Slater determinant, constructed with one-particle orbitals that satisfy the self-consistent field (SCF) equations

$$\left\{ h(i) + \sum_b [\mathcal{F}_b(i) - \mathcal{K}_b(i)] \right\} \phi_n(i) = \epsilon_n \phi_n(i), \quad (2)$$

where \mathcal{F}_b and \mathcal{K}_b are the Coulomb and exchange operators, respectively [4]. Here and in what follows the summation over indices a,b,c run over all occupied states, while n runs over all possible states. The eigenvalues satisfy the relation

$$\epsilon_n = \langle n|h|n \rangle + \sum_b \langle nb||nb \rangle, \quad (3)$$

where $\langle n|h|n \rangle = \int \phi_n(1)^* h(1) \phi_n(1) d1$ are the matrix element of one-particle operator h in the basis $\{\phi_n\}$, and

$$\langle mn||mn \rangle = \langle mn|mn \rangle - \langle mn|nm \rangle, \quad (4)$$

$$\langle mn||pq \rangle = \int \phi_m(1)^* \phi_n(2)^* v(1,2) \phi_p(1) \phi_q(2) d1d2 \quad (5)$$

are the matrix elements of the pair-interaction operator. In the above expression 1 and 2 represent the one-electron variables of coordinate and spin. The energy of the HF state is

$$E_{HF} = \sum_a \langle a|h|a \rangle + \frac{1}{2} \sum_{a,b} \langle ab||ab \rangle = \sum_a \epsilon_a - \frac{1}{2} \sum_{a,b} \langle ab||ab \rangle, \quad (6)$$

where to obtain (6) Eq. (3) is used [4]. The many-particles operator

$$\mathcal{H}_{HF} = \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n - \frac{1}{2} \sum_{a,b} \langle ab||ab \rangle \quad (7)$$

is a natural choice for an approximate independent-particles description of the interacting system. In Eq. (7) \hat{c}_n^\dagger (\hat{c}_n) is the creation (annihilation) operator of a particle in the state ϕ_n . \mathcal{H}_{HF} , known as Hartree-Fock Hamiltonian, is diagonal in the basis of all the Slater determinants composed with the HF orbitals, and its ground state energy is the HF energy E_{HF} . This Hamiltonian operator is the starting point to construct a perturbation expansion for the correlation energy using as perturbation $V_{HF} = \mathcal{H} - \mathcal{H}_{HF}$ [4]. Hence, the energy of the interacting electron system is obtained as a series

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TABLE I. Ground state energies of a system of two harmonically confined spin- $\frac{1}{2}$ particles interacting through a harmonic potential of strength k . Several approximations are included: Hartree-Fock (HF), Møller-Plesset perturbation theory of orders $n=2, 3$ (MP n), modified MP n (MMP n), as well as the exact values. Repulsive interactions are represented by negative values of the elastic constant k .

k	HF	MP2	MP3	MMP2	MMP3	Exact
-0.25	1.732	1.655	1.836	1.702	1.710	1.707
-0.24	1.744	1.681	1.803	1.717	1.724	1.721
-0.22	1.766	1.725	1.784	1.745	1.750	1.748
-0.20	1.789	1.760	1.791	1.772	1.776	1.775
-0.18	1.811	1.791	1.808	1.798	1.801	1.800
-0.16	1.833	1.819	1.828	1.823	1.825	1.825
-0.09	1.908	1.905	1.906	1.905	1.906	1.906
-0.04	1.960	1.959	1.959	1.959	1.959	1.959
-0.01	1.990	1.990	1.990	1.990	1.990	1.990
0.00	2.000	2.000	2.000	2.000	2.000	2.000
0.04	2.040	2.039	2.039	2.039	2.039	2.039
0.16	2.154	2.150	2.149	2.149	2.149	2.149
0.36	2.332	2.319	2.314	2.316	2.313	2.311
0.64	2.561	2.534	2.522	2.525	2.516	2.510
1.00	2.829	2.784	2.762	2.767	2.749	2.732

$$E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + \dots \quad (8)$$

With the choice (7) for the zero-order Hamiltonian, we have that $E^{(0)} = E_{HF}$, and $E^{(1)} = 0$.

A well known feature of the HF theory is that the many body ground state energy E_{HF} is not the bare sum of energies of filled single-particle orbitals. Interactions are counted twice and this overestimation is corrected by subtracting the constant explicit in Eq. (6). A second choice for a Hamiltonian is also possible, however. Equation (6) may be written in the alternative form,

$$E_{HF} = \sum_a \left(\epsilon_a - \frac{1}{2} \sum_b \langle ab || ab \rangle \right), \quad (9)$$

suggesting as an alternative Hamiltonian also diagonal in the HF orbitals

$$\mathcal{H}_{MHF} = \sum_n \tilde{\epsilon}_n \hat{c}_n^\dagger \hat{c}_n, \quad (10)$$

where

$$\tilde{\epsilon}_n = \epsilon_n - \frac{1}{2} \sum_b \langle nb || nb \rangle = \frac{1}{2} (\epsilon_n + \langle n | h | n \rangle). \quad (11)$$

In (10) the operators \hat{c}_n^\dagger and \hat{c}_n are the same as in (7). Hence, \mathcal{H}_{MHF} and \mathcal{H}_{HF} have the same eigenfunctions, and the same ground state energy, but different excitation energies. The correlation energy can again be described in terms of a perturbation, this time of the form $V_{MHF} = \mathcal{H} - \mathcal{H}_{MHF}$. For instance, the second-order correction to the HF ground state energy has the form [4]

$$E^{(2)} = \sum_{\Phi'} \frac{|\langle \Phi | \mathcal{H} | \Phi' \rangle|^2}{E_{HF} - E_{\Phi'}} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab || rs \rangle|^2}{E_{HF} - E_{\Phi'}}. \quad (12)$$

This is the first finite correction in the Rayleigh-Schrödinger perturbation expansion since for either choice of the Hamiltonian the first order term vanishes. Only doubly excited states $\Phi' = \Phi_{ab}^{rs}$ (ϕ_a replaced by ϕ_r and ϕ_b replaced by ϕ_s in the Slater determinant Φ , with ϵ_r, ϵ_s above the Fermi energy) contribute [4]. The choice of the zero-order Hamiltonian affects the excitation energies in the denominator, which have the form

$$E_{HF} - E_{\Phi_{ab}^{rs}} = \begin{cases} \epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s, & \text{if } \mathcal{H}_0 = \mathcal{H}_{HF}, \\ \tilde{\epsilon}_a + \tilde{\epsilon}_b - \tilde{\epsilon}_r - \tilde{\epsilon}_s, & \text{if } \mathcal{H}_0 = \mathcal{H}_{MHF}. \end{cases} \quad (13)$$

Replacing in Eq. (12) both forms clearly lead to different numerical values. The analysis of the third- and higher-order terms in the perturbation expansion yields additional modifications. In the third-order correction $E^{(3)}$, besides the replacements of $\epsilon_m \rightarrow \tilde{\epsilon}_m$ in the standard Møller-Plesset expression [4], an additional term $\Delta E^{(3)}$ appears

$$\Delta E^{(3)} = -E^{(2)} - \frac{1}{4} \sum_{abrs} \frac{(h_{rr} + h_{ss} - h_{aa} - h_{bb}) |\langle ab || rs \rangle|^2}{(\tilde{\epsilon}_r + \tilde{\epsilon}_s - \tilde{\epsilon}_a - \tilde{\epsilon}_b)^2}, \quad (14)$$

where $h_{mn} = \langle n | h | m \rangle$. Curiously, the first element of Eq. (14) cancels the second-order energy correction. Yet, the sum that follows contains the second-order energy as well, with a plus sign, so that $\Delta E^{(3)}$ is third order in the interaction.

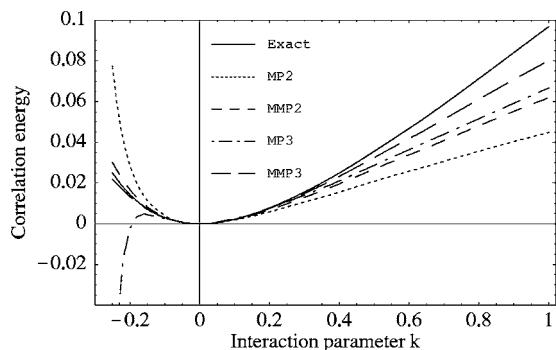


FIG. 1. Correlation energy for a system of two harmonically confined spin-particles interacting through a harmonic potential of strength k . The exact result is included, as well as corrections up to second and third order for the Møller-Plesset (MP) and modified Møller-Plesset (MMP) choices of zeroth-order Hamiltonian.

In order to assess the convenience of either formulation for obtaining the correlation energy we have applied them to two systems of known exact solutions, and for a small number of molecules. The following sections are devoted to this analysis.

II. EXACT MODELS

Our first model system is a two spin- $\frac{1}{2}$ particle in a bidimensional harmonic potential, interacting through a harmonic force. This is an interacting system involving identical fermions that is solved exactly [8]. The Hamiltonian is given by (1) with

$$h(i) = \frac{1}{2}(-\nabla_i^2 + r_i^2), \quad v(i,j) = \frac{1}{2}k(\mathbf{r}_i - \mathbf{r}_j)^2. \quad (15)$$

Here, the coordinates and the energy are given in the oscillator units of the confinement potential. The exact ground state energy is

$$E_0 = 1 + \sqrt{1 + 2k}. \quad (16)$$

The model contains the parameter k that allows the study of attractive ($k > 0$) as well as repulsive ($k < 0$) interactions. Equation (16) shows that $k = -0.5$ is the lowest value for which a bound state exists.

To obtain a numerical solution at the Hartree-Fock level, we use a basis of noninteracting harmonic oscillators eigenfunctions

$$\phi_{n_x, n_y}(x, y) = \varphi_{n_x}(x)\varphi_{n_y}(y), \quad 0 \leq n_x + n_y \leq 5, \quad (17)$$

where the $\varphi(x)$ are the usual one-dimensional harmonic oscillator eigenfunctions. The set (17) is an exact solution when $k=0$. The HF solution is obtained by solving the SCF equations (2) in a spin restricted configuration, i.e., constraining the spatial part of the wave function to be equal for the two occupied states with opposite spins [4].

Table I shows the ground state energy for the Hamiltonian (15) calculated using the standard Møller-Plesset perturbation theory of order $n=2, 3$ (MP n), and our modified form, MMP n . Figure 1 shows the exact correlation energy $E_{corr} = E_{HF} - E$ for different values of k , together with results ob-

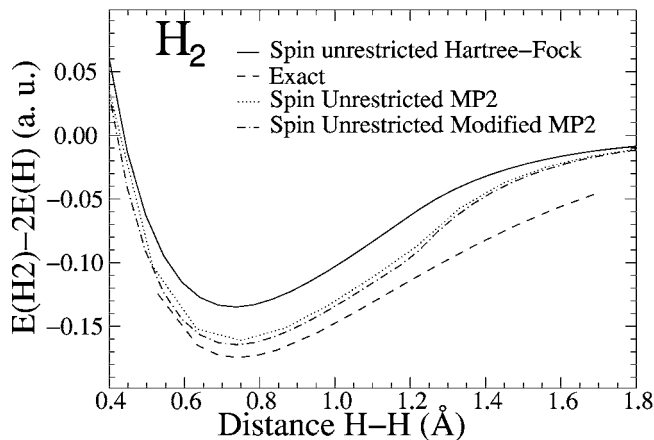
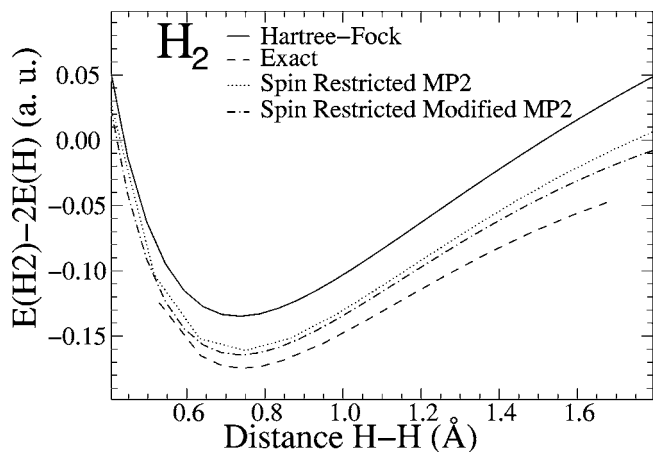


FIG. 2. Potential energy surface for the H_2 molecule as a function of the distance H-H. The basis set used is 6-31G^{**}. Top: spin-restricted configuration. Bottom: spin-unrestricted configuration.

tained for the two choices of the HF Hamiltonian, in the second and third order of the perturbation theory. Notice that MMP n yields better results throughout. Notice also that the usual MP n fails poorly in both orders of approximation when the system becomes more loosely bound, as k approaches the critical value -0.5 . In fact, convergence problems prevent solving the HF SCF equations for k beyond -0.25 . By contrast, the MMP n continue to be good approximations even in this range of k .

The simplest molecular system is the hydrogen molecule, for which we present the *potential energy surface* (PES) in both spin restricted and unrestricted configurations [8]. The

TABLE II. Bondlengths (in pm) of diatomic molecules and the error made in different approximations. The basis used is cc-pVTZ.

	Exp	HF	MP2	MMP2	B3LYP
H_2	74.1	-0.7	-0.4	-0.2	+0.2
HF	91.7	-1.9	+0.03	-1.6	+0.5
OH^+	102.9	-2.2	-0.5	-1.6	+1.0
NH	103.6	-1.9	-0.9	-1.7	+0.3
NO^+	106.3	-3.6	+1.5	+2.7	-0.6
BH	123.2	-1.0	-1.5	-0.8	+0.0

TABLE III. Correlation energy (in atomic units) for several diatomic molecules at the experimental bondlengths. The basis used is cc-pVTZ.

	EHF	MP2	MP3	MMP2	MMP3	CI
H ₂	-1.133	-0.032	-0.037	-0.034	-0.038	-0.039
HF	-100.058	-0.290	-0.290	-0.228	-0.268	-0.282
C ₂	-75.402	-0.385	-0.347	-0.328	-0.346	-0.407
NH	-54.875	-0.172	-0.191	-0.149	-0.179	-0.207
NO ⁺	-128.966	-0.439	-0.422	-0.369	-0.408	-0.445
OH ⁺	-74.866	-0.182	-0.202	-0.156	-0.189	-0.222
BH	-25.130	-0.084	-0.101	-0.077	-0.095	-0.110

molecular electronic Hamiltonian in atomic units is given by (1) with

$$h(i) = -\frac{1}{2}\nabla_i^2, \quad v(i,j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (18)$$

The HF wave functions are obtained by the expansion in standard basis sets of Gaussian functions [4] (e.g., 6-31G^{**}, DZP, etc.) and applying the SCF method as implemented in the code HONDO [9]. The MMP2 and MMP3 energies are obtained by a minor modification of the MP2 and MP3 routines in the same code.

The PES of H₂ has been calculated by Kolos and Wolniewicz [10] with extreme precision and can be regarded as exact, thus allowing a reference for approximative methods. It can be seen in Fig. 2 that the MMP2 method improves the correlation energy over the standard MP2 in the whole range of distances. A well known failure of the spin restricted HF and derived methods is the inability to describe the dissociation of the molecule, as the two occupied states must have the same orbital wave function. This problem is solved by the spin-unrestricted HF method, where the restriction that opposite spin orbitals share the orbital part is lifted. Again, our modified scheme provides a solution closer to the exact one to second order. However, it can be appreciated that for unrestricted calculations both the MMP2 and MP2 are worse than the restricted case in the range 1.2–1.6 Å. This shows that the problem of spin contamination affects both MP2 and MMP2.

III. MOLECULAR SYSTEMS

In this section, we evaluate the MMP approximation for several simple molecules, for which no exact wave functions are known. Table II shows the error made at the second order of approximation in the bondlength of a set of diatomic molecules, as compared with the experimental length. It can be appreciated that the bondlength is improved by the perturbation schemes saved for BH, where the MP2 increases the error. MMP2 gives better results for H₂ and BH, while MP2 is more accurate in the other cases. For reference, the results with the popular density functional method B3LYP are included in the table.

Next, we turn our attention to the value of the correlation energy at the experimental geometries. Tables III and IV show a comparison of the standard MP n energies with the present MMP n energies. For reference and comparison, the values with the most accurate configuration interaction (CI) quantum chemistry method are included. For these molecules it turns out that the correlation energy is, in general, better in MP n than in MMP n methods. Only for the symmetric pairs the methods are comparable, MMP n giving a slightly better result for H₂.

The reason for the rather low correlation energy in the MMP2 can be explained in terms of Eqs. (12) and (13). It corresponds to an increase of the energy gap between the occupied and unoccupied states. This can be appreciated in Fig. 3, where the Fock eigenvalues (3) and the modified eigenvalues (11) for the HF are shown. As can be noticed, the correction to the Fock eigenvalues is greater for the (dou-

TABLE IV. Calculated energies (in atomic units) for several diatomic and triatomic molecules at the experimental geometries. Geometries and basis functions are specified as follows: BH: $r=2.329 a_0$, DZP. HF: $r=1.733 a_0$, DZP. CH₂: $r=2.11 a_0$, $\theta=102.4^\circ$, DZP. H₂O: $r=1.88973 a_0$, $\theta=104.5^\circ$, DZP. NH₃: $r=1.91165 a_0$, $\theta=106.7^\circ$, DZV. a_0 : Bohr radius, DZV: Dunning's (9s,5p)/(3s,2p) basis set, DZP: DZV plus polarization.

	EHF	MP2	MP3	MMP2	MMP3	CI
BH	-25.124	-25.183	-25.199	-25.187	-25.198	-25.209
HF	-100.048	-100.232	-100.233	-100.186	-100.220	-100.251
CH ₂	-38.885	-38.998	-39.017	-38.992	-39.013	-39.027
H ₂ O	-76.041	-76.242	-76.247	-76.200	-76.234	-76.254
NH ₃	-56.176	-56.290	-56.297	-56.268	-56.289	-56.304

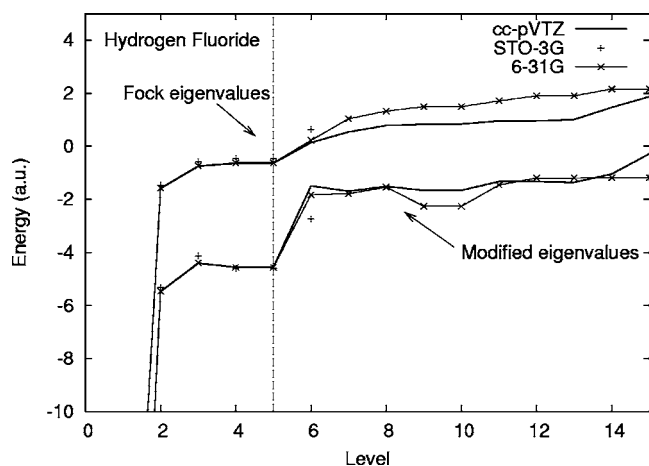


FIG. 3. Fock eigenvalues (upper group) and modified eigenvalues (lowest group) of the molecule HF, calculated with different basis sets: STO-3G, 6-31G, and cc-pVTZ. The lines are guides to the eyes. The dashed vertical line indicates the highest occupied molecular orbital.

bly) occupied levels (level ≤ 5) than for the unoccupied ones. This is related to the values of the interaction integrals $\langle nb|nb \rangle$ present in Eq. (11). These integrals are generally positive and have larger values for the occupied levels because the corresponding orbitals ϕ_n have more overlap with the occupied orbitals (ϕ_b). For example, in hydrogen fluoride the occupied orbitals are concentrated around the F atom, while the lowest unoccupied molecular orbital and higher molecular orbitals are more dense around the H atom. For the C_2 molecule the effect is less pronounced though qualitatively similar.

The case of H_2 and the two-fermion oscillator is different. In this case, there are only two occupied states with the same energy, and the sum over the b states in Eq. (11) contains only one term, as $\langle nn|nn \rangle = 0$. On the other hand, for the unoccupied states the b sum contains two terms and the negative shift of these eigenvalues is larger, thus reducing the gap. This effect is also present in larger molecules, but it is overcome by the differences in the spatial distribution of the wave functions, as discussed above.

IV. CONCLUSIONS

We have proposed and analyzed critically an alternative formulation of the Møller-Plesset perturbation series for the ground state of many-particle fermion systems. The new zeroth-order Hamiltonian has the same wave functions as the Hartree-Fock Hamiltonian, but with a different spectrum. Here, the correction to obtain the correct Hartree-Fock energy is included in the single-particle energies, instead of through a global energy shift. This opens a possibility of including part of the correlation energy in the zero-order Hamiltonian, correcting at the same time for the well known double count of the interaction energy present in the ordinary Hartree-Fock formulation. We have applied the new method to a number of different systems and have found that the new method is as good or better than the Møller-Plesset scheme in symmetric systems. However, for molecular systems with more than two electrons, the standard MP series seems to provide better accuracy. It turns out that the correction to the one-particle energy levels is larger for the occupied levels than for the unoccupied ones, increasing the gap between occupied and unoccupied states. This reduces the size of the lowest-order contributions to the correlation energy, decreasing the rate of convergence of the perturbation series. However, we note that in order to obtain the HF energy in the zero-order approximation to the many-particles problem, Eq. (11) needs to be applied only to the occupied HF states. We stress that this choice is motivated by the attempt to eliminate the double counting of the mean field interaction energies in the HF energy. There is no reason other than simplicity to apply the same scheme to the empty levels. This degree of freedom could be exploited to improve the convergence of the many-particles perturbation series.

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