

A Guided Stochastic Energy-Domain Formulation of the Second Order Møller–Plesset Perturbation Theory

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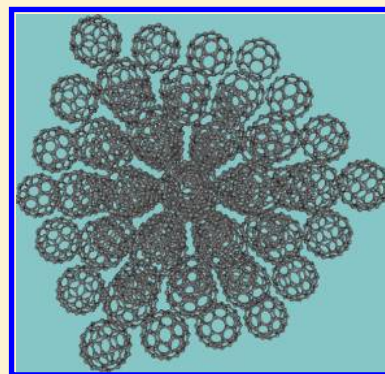
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ABSTRACT: We develop an alternative formulation in the energy-domain to calculate the second order Møller–Plesset (MP2) perturbation energies. The approach is based on repeatedly choosing four random energies using a nonseparable guiding function, filtering four random orbitals at these energies, and averaging the resulting Coulomb matrix elements to obtain a statistical estimate of the MP2 correlation energy. In contrast to our time-domain formulation, the present approach is useful for both quantum chemistry and real-space/plane wave basis sets. The scaling of the MP2 calculation is roughly linear with system size, providing a useful tool to study dispersion energies in large systems. This is demonstrated on a structure of 64 fullerenes within the SZ basis as well as on silicon nanocrystals using real-space grids.



SECTION: Molecular Structure, Quantum Chemistry, and General Theory

The second order Møller–Plesset (MP2) perturbation theory is one of the simplest and most fundamental forms used to introduce correlations in electronic structure calculations.¹ The formal MP2 expression can be manipulated into the following manifestly negative-definite form:

$$E_{\text{MP2}} = - \sum_{ijab} \frac{\langle ab|ij\rangle^2 + \langle ab|ji\rangle^2 - \langle ab|ij\rangle\langle ij|ab\rangle}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j} \quad (1)$$

where $\langle ab|ij\rangle$ and $\langle ab|ji\rangle$ are the Coulomb and exchange matrix elements, respectively, ϵ_i is the orbital energy, and the indices ij and ab refer to occupied and virtual states, respectively. Direct application of eq 1 involves CPU time scaling as $O(N^5)$ with the size of system (N). Such scaling severely caps the size of systems which can be studied and serves as a driving force to develop more efficient computational schemes.^{2–12} In these methods, linear scaling emerges once the system is larger than the one particle density matrix range, typically above a few tens of thousands of atoms, limiting the efficacy of the methods considerably.

In a previous paper¹³ we developed an expeditious stochastic approach to obtain the MP2 energy, whereby the energy denominator in eq 1 is replaced by integration over a real-time correlation function and the exact eigenstates are replaced by arbitrary combinations of random states filtered to be in the occupied and virtual space, respectively. Application to hydrogen passivated silicon nanocrystals with thousands of electrons represented on a real-space grid provided accurate

estimates of the MP2 energies in systems far beyond the capabilities of present day MP2 implementations.

Here we present an alternative stochastic approach, akin to our previous work on multiexciton generation rates,¹⁴ more suitable for quantum chemistry basis-sets and applicable also to exact exchange in the Hamiltonian. The approach is based on choosing four random energies using a nonseparable guiding function and then filtering four random orbitals at these energies. The MP2 energy is then estimated as an average over different combinations of random orbitals, where for each combination we calculate the contribution to the MP2 energy given by eq 1 with a proper weight.

Other stochastic schemes have been recently proposed to reduce the computational workload of calculating electron correlations.^{15–17} Of particular relevance to the present work are the graph random walk in the atomic basis set space¹⁸ and a stochastically sampling of the electron-position space¹⁹ to obtain the MP2 correlation energy. Our approach is different in that we use stochastic orbitals and as such, the resulting MP2 approach can be used to handle huge systems.

The motivation for the development of the present energy-domain method is to avoid the costly repeated estimates of the Coulomb matrix elements in the time-domain formulation. In real-space/plane-wave basis, this is relatively cheap, but when quantum-chemistry basis sets are used, the estimation of the

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Table 1. MP2 Energies (Per Electron, in eV) Using Siesta Basis Sets with the Stochastic Energy-Domain Approach for a Range of Molecules, up to Clusters of 36 and 64 Fullerenes (with Center-to-Center Distances of 10 Angstrom)^a

molecule	N_e	basis set	M	I	E_{MP2}/N_e		$SE/ E_{\text{MP2}} $	$SE_1/ E_{\text{MP2}} $	guiding function?
					deterministic	stochastic			
water	8	SZ	6	1048576	-0.197	-0.196	1.02%	7.65	N
	8	DZVP	23	1048576	-1.015	-1.029	1.17%	12.24	N
ethylene	12	SZ	12	4194304	-0.447	-0.454	1.32%	27.97	N
	30	SZ	30	4194304	-0.521	-0.523	0.96%	21.22	N
benzene	30	SZ	30	1048576	-0.521	-0.522	0.96%	10.73	Y
	48	SZ	48	1048576	-0.558	-0.557	0.72%	8.08	Y
Pentacene	102	SZ	102	1048576		-0.560	0.71%	6.61	Y
catechol–fullerene	290	SZ	286	524288		-0.709	0.56%	3.81	Y
	290	DZ	572	524288		-0.995	0.50%	3.62	Y
	290	DZVP	940	524288		-1.442	0.62%	4.71	Y
fullerene	240	SZ	240	1048576		-0.678	0.44%	3.98	Y
	240	DZ	480	1048576		-0.981	0.51%	5.20	Y
	240	DZVP	780	1048576		-1.434	0.49%	4.95	Y
fullerene 3 × 3 × 4	8640	SZ	8640	131072		-0.704	0.85%	3.12	Y
fullerene 4 × 4 × 4	15360	SZ	15360	65536		-0.696	1.15%	2.87	Y

^aFor small molecules we compare the stochastic results with the traditional explicit summation results. We plot the error relative to the total energy, as well as the relative per-iteration error. Catechol–fullerene refers to a fullerene derivative with a catechol molecule fused to an open fullerene cage through a 2-carbon linker.

Coulomb integral at each time step becomes the most demanding portion of the calculation, and thus, prohibits application to large systems. In contrast, the energy-domain formulation requires the evaluation of a single Coulomb integral for each set of random orbitals, providing a framework for a stochastic MP2 approach suitable for quantum chemistry basis sets.

To start, let us note the following relation, replacing a sum over states by an average $\langle \dots \rangle_{\chi}$ over random orbitals $\chi_i(\mathbf{r})$:

$$\sum_{i \in \text{occ}} f(\varepsilon_i) \langle i | \hat{A} | i \rangle = \int f(\varepsilon) \langle i_{\varepsilon} | \hat{A} | i_{\varepsilon} \rangle_{\chi} d\varepsilon \quad (2)$$

where:

$$i(\mathbf{r}) \equiv i_{\varepsilon}(\mathbf{r}) = \theta(\mu - \varepsilon) \sqrt{\frac{\delta_{\sigma}(\varepsilon - H)}{\rho(\varepsilon)}} \chi_i(\mathbf{r}) \quad (3)$$

is a “projected” random occupied orbital at energy ε , $\delta_{\sigma}(\varepsilon) = (2/\pi) \{ \sigma^3 / [\pi(\varepsilon^2 + \sigma^2)]^2 \}$ is a squared Lorentzian filter function, $\rho(\varepsilon) = \text{tr}(\varepsilon - H)$ is the density of states (DOS), $\theta(x)$ is the Heaviside step function, and μ is the chemical potential. Similarly, for a virtual orbital we have an analogous expression with the following random orbitals:

$$a(\mathbf{r}) \equiv a_{\varepsilon}(\mathbf{r}) = \theta(\varepsilon - \mu) \sqrt{\frac{\delta_{\sigma}(\varepsilon - H)}{\rho(\varepsilon)}} \chi_a(\mathbf{r}) \quad (4)$$

With this notation, the MP2 energy can be written as

$$E_{\text{MP2}} = - \int \frac{V^2(\{\varepsilon\})}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} p(\{\varepsilon\}) d^4\{\varepsilon\} \quad (5)$$

where $\{\varepsilon\}$ is shorthand notation for $\{\varepsilon_a, \varepsilon_b, \varepsilon_i, \varepsilon_j\}$ and $\{\chi\}$ for $\{\chi_a, \chi_b, \chi_i, \chi_j\}$, $p(\{\varepsilon\}) = \rho(\varepsilon_a) \rho(\varepsilon_b) \rho(\varepsilon_i) \rho(\varepsilon_j)$, and the manifestly positive definite coupling $V^2(\{\varepsilon\}) = \langle \langle ab|ij \rangle^2 + \langle ab|ji \rangle^2 - \langle ab|ij \rangle \langle ij|ab \rangle \rangle_{\{\chi\}}$. The integrand in eq 5 has contributions from the Coulomb matrix elements, which depend on the ε 's and the density of states, and the denominator, which also depends on the ε 's in an obvious way. To perform the integral, we need to

evaluate it using a Monte Carlo procedure with importance sampling based on a guiding function $w(\{\varepsilon\})$:

$$E_{\text{MP2}} = - \int \frac{V^2(\{\varepsilon\}) p(\{\varepsilon\})}{(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j) w(\{\varepsilon\})} w(\{\varepsilon\}) d^4\{\varepsilon\} \quad (6)$$

Note that all contributions to the integral are positive definite; this is guaranteed by the form used in eq 1 instead of the typical form involving $2\langle ab|ij \rangle^2 - \langle ab|ij \rangle \langle ij|ab \rangle$, which is not positive definite.

We find that a guiding weight of the form

$$w(\{\varepsilon\}) = p(\{\varepsilon\}) (\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j)^{-\alpha} \times \left(\frac{1}{((\varepsilon_a - \varepsilon_i) - (\varepsilon_b - \varepsilon_j))^2 + \beta^2} + \frac{1}{((\varepsilon_a - \varepsilon_j) - (\varepsilon_b - \varepsilon_i))^2 + \beta^2} \right) \quad (7)$$

works quite well and the numerical fluctuations are fairly insensitive to the values of β (chosen here as $\beta^2 = 1/100$ and $\alpha = 3$). This function accounts for the fact that the coupling matrix elements tend to be large whenever the particle-hole pairs are close in energy, i.e., whenever $\varepsilon_b - \varepsilon_i \approx \varepsilon_a - \varepsilon_j$ or $\varepsilon_b - \varepsilon_j \approx \varepsilon_a - \varepsilon_i$.

We applied the energy-domain formalism using an atomic basis set, where the $M \times M$ overlap and Hamiltonian matrices, S and H (M is the size of the basis) are transformed to an orthogonal basis, $\tilde{H} = S^{-1/2} H S^{-1/2}$ and then we diagonalize $\tilde{H} = U \varepsilon U^T$. The density of states is constructed explicitly from the eigenvalues of \tilde{H} , e.g.:

$$\rho(\varepsilon) = \sum_{s=1}^M \delta_{\sigma}(\varepsilon - \varepsilon_s) \quad (8)$$

Then, in each iteration we randomly sample four energies from the weight function $w(\{\varepsilon\})$ and also choose four sets of random coefficients (with respect to the basis set), χ_s , that yield

the four random orbitals. The coefficients are uniformly generated in the range $-\sqrt{3} < \chi_s < \sqrt{3}$ where $s = 1, \dots, M$. This choice ensures that the components of the random vectors are mutually orthonormal on average, i.e., $\langle \chi_s \chi_t \rangle_\chi = \delta_{st}$. The four random orbitals are then filtered, e.g., when the energy is smaller than μ one obtains an occupied random orbital:

$$(\bar{\tau}_\varepsilon)_s = \sqrt{\frac{\delta_\sigma(\varepsilon - \varepsilon_s)}{\rho(\varepsilon)}} \chi_s \quad (9)$$

Similarly, for a virtual random orbital one obtains

$$(\bar{\tau}_\varepsilon)_a = \sqrt{\frac{\delta_\sigma(\varepsilon - \varepsilon_a)}{\rho(\varepsilon)}} \chi_a \quad (10)$$

The four orbital are then rotated to the original atomic basis, $i_\varepsilon = S^{-(1)/(2)} U \bar{\tau}(\varepsilon)$ and $a_\varepsilon = S^{-(1)/(2)} U \bar{a}(\varepsilon)$. Finally, the two-electron integrals $\langle ijlab \rangle$ involving the four random orbitals are performed on a 3D real-space grid, applying Fast Fourier techniques for the convolution operation.

There are several sources for numerical errors in estimation of the MP2 energy in a given basis. The systematic errors result from the parameter σ in the squared-Lorentzian, but this can be controlled to a desired predefined accuracy; we found by studying a host of molecules (up to and including fullerene) that as long as $\sigma \leq 0.5$ eV (the value used), the results are independent of σ to better than 0.2% (i.e., within the stochastic errors in our simulations). Stochastic errors (SE) are due to random fluctuations and can be controlled by repeated sampling. After I samplings (iterations) the SE is equal to SE_1/\sqrt{I} , where SE_1 is the standard deviation of the results, which we also label below as the “SE per iteration”. Finally, there are numerical errors associated with the evaluation of the two-electron integrals. Here, the basis set integrals are evaluated by representing the wave functions on a real-space grid and using a convolution to obtain $V^2(\{\varepsilon\})$. This can be controlled by increasing the grid size or, alternatively, to obtain the two-electron integrals by a more accurate approach based on the tensor hypercontraction.¹²

We now describe applications of the method for small and medium sized molecules, and for huge fullerene clusters (with 36 and 64 fullerenes) with over 15 000 basis functions. We used the Siesta package²⁰ within the SZ, DZ, and DZVP Siesta numerical atomic basis sets. The results of these MP2 energy calculations are summarized in Table 1. For small molecules, we compare the results of the stochastic calculations with the explicit summation results of eq 1, referred to as “deterministic”. We provide details about the basis set used, the total number of basis function, the number of stochastic sets of orbitals used (iterations), the relative statistical error in the MP2 energy per electron (SE/E_{MP2}), the standard error per iteration SE_1/E_{MP2} (related to the error as $SE = SE_1/\sqrt{I}$ and whether a guiding weight function was used or not.

We find that the MP2 correlation energy per electron is roughly independent of the system size for systems with similar electronic character. This is certainly the case for benzene, naphthalene, and pentacene series ($|E_{MP2}|/N_e \approx 0.56$ eV) and also for varying sizes of fullerene clusters ($|E_{MP2}|/N_e \approx 0.68 - 0.70$ eV).

The SE per iteration decreases somewhat with the size of the system. For example, the SE per iteration decreases from 2.7 to 2.0 eV when a fullerene is replaced by a fullerene cluster. Similarly, the SE per iteration decreases from 5.6 to 3.7 eV

when going from benzene to pentacene. This is in contrast to the time-domain algorithm, where the SE decreased and then leveled off for a linear chain model and increased and leveled off for a 3D silicon nanocrystal (see more below). The reduction of the SE per iteration indicates that the energy formulation of MP2 benefits from self-averaging, again in contrast to the time-domain approach. Furthermore, as the basis increases, the SE per iteration increases from 2.7 eV to 7.1 eV, which is natural since the MP2 energy also increases by a similar factor.

In Table 2 we show in more detail the effect of the guiding function on the SE for a set of molecules. It reduces the SE per

Table 2. The Effects of the Guiding Function on the Per Iteration Error (i.e., the Standard Deviation), Measured Relative to the Overall MP2 Energy^a

molecule	basis set	guiding function?	E_{MP2}/N_e	$SE_1/ E_{MP2} $
benzene	SZ	N	-0.518	19.3
		Y	-0.522	9.6
naphthalene	SZ	N	-0.548	16.0
		Y	-0.557	7.2
pentacene	SZ	N	-0.583	25.7
		Y	-0.560	7.1
fullerene	SZ	N	-0.700	11.4
		Y	-0.678	4.4
	DZ	N	-0.972	13.4
		Y	-0.980	5.1
	DZVP	N	-1.448	15.9
		Y	-1.433	4.9

^aThe guiding function reduces the statistical error by a factor of 2–4.

iteration by approximately 2 for the smallest molecule and nearly a factor of 4 for the largest, implying reduction of the number of stochastic orbitals required to achieve a given SE by a factor of 4 for smaller molecules and 16 for larger ones.

The overall computational time in hours (T_{comp}) of the MP2 step on a single 2.5 GHz CPU is well approximated by the following combination of the overlap integrals and vector preparation:

$$T_{\text{comp}} \sim 2 \times 10^{-8} IM \log_2 M + 4 \times 10^{-13} IM^2$$

In practice, the first quasi-linear term (overlap-integrals) dominates the calculation time for $M < 10^6$. For the 36- and 64-fullerene clusters with 131 000 and 65 000 iterations, respectively, $T_{\text{comp}} = 300$ h.

The principles of our energy-domain stochastic approach can also be applied to a real-space-grid or plane-waves representation. Here, the underlying basis is orthogonal, so there is no overlap matrix to consider; on the other hand, the Hamiltonian matrix is too large to be diagonalized, and so iterative sparse matrix techniques must be applied. The random orbitals (cf. eqs 3 and 4 can be obtained similarly to ref 13 by representing $[\delta_\sigma(\varepsilon - H)]^{1/2}$ as a Gaussian (instead of a Lorentzian) and expanding in a Chebyshev series of length N_c .²¹ From the structure of the Chebyshev series, it is possible to obtain several stochastic orbitals of different ε from a single expansion, and we use this property to obtain 4 unoccupied and 16 occupied orbitals. In addition, the density of states $\rho(\varepsilon)$ is calculated separately using a stochastic trace formula as in ref 14. Finally, the two electron integrals for the orbitals on the grid are obtained here also using fast Fourier convolution techniques.

We apply the energy-domain stochastic method to hydrogen passivated spherical silicon nanocrystals (NCs) of several sizes. We use a semiempirical pseudopotential model to construct the single particle Hamiltonian²² and a real-space grid to represent the single particle orbitals.²³ In Table 3 we summarize the

Table 3. Comparison between the Energy (Present) and Time (Ref 13) Domain Stochastic MP2 Calculations for Hydrogen Passivated Silicon Nanocrystals^a

nanocrystal:		Si ₃₅ H ₃₆	Si ₈₇ H ₇₆	Si ₃₅₃ H ₁₉₆
N_e		176	424	1608
M		32768	110592	262144
E_{MP2}/N_e	energy-domain	-1.03	-1.07	-1.23
	time-domain	-1.06	-1.13	-1.31
$SE/ E_{MP2} $	energy-domain	0.03	0.04	0.04
	time-domain	0.02	0.03	0.04
$SE_1/ E_{MP2} $	energy-domain	6.8	8.7	8.6
	time-domain	0.8	1.3	1.8
ratio of computational work (energy/time-domain)		4.8	3.3	1.4

^aThe number of stochastic orbitals used is 50 000 for the energy-domain results and 2500 for the time-domain results.

results for three systems sizes: Si₃₅H₃₆, Si₈₇H₇₆, and Si₃₅₃H₁₉₆. The total number of electrons varies from 176 to 1608, and the size of the Hamiltonian matrix varies from 32³ to 64³. Since a direct calculation of the MP2 correlation energy is prohibited for these NCs, we compare the current approach to our previous time-domain stochastic approach.¹³

The agreement between the energy- and time-domain stochastic approaches is excellent for the smaller NCs (differences are well within the SE). For the largest NC, we find small deviations between the two approaches, which may result from systematic errors introduced by the finite width used to represent the filtering function, $[\delta_\sigma(\epsilon - H)]^{1/2} = [1/(2\pi\sigma^2)^{1/2}]e^{-(\epsilon-H)^2/2\sigma^2}$. σ needs to be adjusted according to the density of states. If σ is too large, then the filtered states will contain contributions from occupied and virtual orbitals, which will lead to a large systematic error. If σ is too small, then each filter will generate a single eigenstate of the Hamiltonian, and the SE will be large. Table 4 shows the results for different

Table 4. The MP2 Correlation Energy and SE for Si₃₅H₃₆ for Different Values of the Chebyshev Expansion Length

expansion length N_c :	500	1000	2000
value of σ (eV)	1.44	0.72	0.36
stochastic MP2 energy per electron (eV)	-1.07	-1.07	-1.03
relative error $SE/ E_{MP2} $	0.04	0.03	0.03
relative error per iteration $SE_1/ E_{MP2} $	9.2	7.1	7.3

Chebyshev expansion lengths corresponding to different values of $\sigma \approx (2.5/\sqrt{2})(\Delta E/N_c)$, where ΔE is the energy range of the Hamiltonian H . For the set of σ chosen, all results converge to the same MP2 correlation energy with a similar SE. Larger NC, however, may require a longer Chebyshev expansion since the quasi-particle gap is smaller by nearly a factor of 2 compared to the smaller NC.

It is interesting to note that the SE per iteration in the energy-domain calculations, which does not incorporate the guiding function, are much larger in comparison to the time-domain approach. However, since the time-domain approach

requires in addition to the filtering step, a propagation step, the overall ratio of computational work is between 1.4 and 4.8 depending on the size of the NC. For the larger NC, this ratio should be multiplied by 2 if an appropriate length of the Chebyshev expansion is used. On the other hand, we did not use a guiding function in these calculations, and that would have allowed us to reduce the energy-domain computational effort by a factor of 2–4 based on the results reported in Table 2.

To summarize, we developed an energy-domain stochastic method for estimating the MP2 energy which gives converged per-electron properties. For a basis of localized atomic orbitals, e.g., contracted Gaussian functions (CGF), the energy-domain approach is more suitable than our previous time-domain approach. A key element is the introduction of a guiding function which we find to reduce the computational effort by a factor of 4–16. The approach is also suitable for a real-space-grid or plane-waves representation where the time-domain approach seems more suitable, but the energy-domain approach seems to work nearly as fast when the system size increases.

Our results show that it is feasible to perform MP2 correlation energy calculations even for very large systems. For atomic basis sets, assuming that the Hartree–Fock orbitals and orbital energies are available, our MP2 approach scales as $O(N \log N)$. In the real-space-grid or plane-waves application the unoccupied orbitals and energies are not known and we rely on application of filters to random wave functions (applied using Chebyshev expansions), and the scaling is also $O(N \log N)$. Finally, we note that the calculations reported here are for the total energy per electron and not for energy differences. Future directions will involve the development of a scheme to obtain the correlation energy differences using the adiabatic approach similar to the stochastic random phase approximation of ref 15.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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