

Elimination of energy denominators in Møller–Plesset perturbation theory by a Laplace transform approach

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It is shown how the energy denominators encountered in various schemes for electronic structure calculation can be removed by a Laplace transform technique. The method is applicable to a wide variety of electronic structure calculations.

Recent development of direct methods for electronic structure calculations [1–4] has allowed the application of rigorous ab initio theory to molecules of a size which was unthinkable only a few years ago. SCF calculations are now possible on systems with nearly 2000 basis functions [5,6], and even at the correlated level, very large basis sets are routinely being used. [7] The bottleneck in these correlated calculations is usually the storage and manipulation of integrals in an MO basis, rather than the CPU time. Especially in extended systems, the information contained in these integrals could be substantially compressed if the orbitals were localized, with a resulting saving in the storage requirement. Localization of orbitals may also be advantageous from other points of view, e.g. for reducing basis set superposition errors [8]. However, many schemes for electron correlation place restrictions on such orbital localization, and a deviation from canonical orbitals often requires the use of iterative schemes [8–10].

We suggest here an elementary but useful treatment based on a Laplace transform, which is applicable to a wide variety of electronic structure calculations whenever energy denominators are encountered. Second-order perturbation theory may suffice as one simple illustration of the technique:

In a spin-orbital formalism, the second-order correction to the electronic energy can be written as

$$E^{(2)} = -\frac{1}{4} \sum_{ijab} \frac{\langle ab || ij \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (1)$$

where $\langle ab || ij \rangle = \langle ab | ij \rangle - \langle ab | ji \rangle$, and

$$\langle ab | ij \rangle = \int \psi_a(1) \psi_b(2) \frac{1}{r_{12}} \psi_i(1) \psi_j(2) dx_1 dx_2$$

(spin integration). (2)

As usual, i, j, \dots in (1) denote occupied MOs, and a, b, \dots the virtuals. By introducing a Laplace transform for the denominator in (1),

$$(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)^{-1} = \int_0^\infty \exp[-(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t] dt, \quad (3)$$

one obtains

$$E^{(2)} = -\frac{1}{4} \int_0^\infty dt \sum_{ijab} \langle ab || ij \rangle^2 \times \exp[-(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t]. \quad (4)$$

The t -dependence of the integrand can now be transferred to the orbitals,

$$\psi_i(t) = \psi_i(0) \exp(\frac{1}{2}\epsilon_i t)$$

for the occupied orbitals (and zero for virtuals), (5a)

$$\psi_a(t) = \psi_a(0) \exp(-\frac{1}{2}\epsilon_a t)$$

for the virtuals (zero for occupied), (5b)

after which the correlation energy takes the form

$$E^{(2)} = \int_0^{\infty} e^{(2)}(t) dt, \quad (6)$$

where

$$e^{(2)}(t) = -\frac{1}{4} \sum_{ij,ab} \langle a(t)b(t) | |i(t)j(t)\rangle^2. \quad (7)$$

The significance of the above lies in the fact that a canonical representation is no longer required when the sum over pairs in (7) is carried out. Due to the generalized definition of the orbitals, the summations need not be restricted to any particular subspaces. This leaves some additional flexibility in defining different types of orbital rotations for computational convenience. One may, for instance, define rotations of the orbital spaces by means of various unitary matrices,

$$\psi_i = \sum_t^{N_{\text{bas}}} \phi_t U_{ti}, \quad (8a)$$

$$\phi_t = \sum_I^{N_{\text{bas}}} \psi_I U_{tI}, \quad (8b)$$

where the matrices U for the transformations of the indices are unitary. This trivially leads to

$$\begin{aligned} e^{(2)} &= -\frac{1}{4} \sum_{ij,ab} \sum_{II'} \langle ab || Ij \rangle \langle I'j || ab \rangle U_{ii'} U_{tI'} \\ &= -\frac{1}{4} \sum_{Ij,ab} \langle ab || Ij \rangle^2, \end{aligned} \quad (9)$$

and similarly for transformation of the other indices. There exist several important classes of unitary rotations of the orbital space for which (7) is invariant. These include separate orbital rotations applied to the four indices i, j, a, b , different rotations for different t values, etc. Note that the set of $\psi(t)$ are not normalized; therefore, even a "unitary" ($N_{\text{occ}} \times N_{\text{occ}}$) rotation in the occupied space leaves the ϕ non-orthogonal. However, U does not need to have an occupied-virtual blocked structure. Any unitary U would suffice, which opens the possibility for using non-orthogonal orbitals within the current scheme.

Schemes employing localized or non-orthogonal orbitals can, therefore, readily be implemented. This is especially attractive in very large systems where one cannot store even the transformed integrals $\langle ij || ab \rangle$ in a canonical basis. Localization significantly increases the sparsity of the transformed in-

tegrals, thereby reducing the storage requirement. Non-orthogonality is important in this context in order to remove the localization tails.

The integral in (6) must be evaluated numerically. This is not a major obstacle, however, since $e^{(2)}(t)$ is a quite well-behaved, monotonically decreasing function. With logarithmically spaced quadrature points, no more than 10–15 points are required to obtain accuracy at the micro-hartree level. Especially with localized orbitals in extended systems, the price paid for the repeated evaluation of $e^{(2)}(t)$ at different values of t is often more than offset by the much smaller "effective" orbital spaces needed in a localized picture.

To summarize, it is shown how the energy denominators in perturbation theory, which preclude localization and other types of orbital rotations, can be replaced by a numerical integration over an auxiliary variable. The rotations made possible by such a technique are not restricted to simple unitary rotations within the occupied orbital space. Second-order perturbation theory is chosen as a simple example to illustrate the technique. The approach is quite general, however, and can be applied to higher orders of perturbation theory as well as to other types of correlation treatment where energy denominators occur.

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