A rigorous upper bound energy for the unitary coupled electron pair approximation method

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Hoffmann and the author recently developed an *ab initio* quantum chemistry method[1] which they labeled the unitary coupled-electron-pair (UCEPA) method. This approach (i) can provide size-extensive energies, (ii) admits a multiconfigurational reference function, and (iii) can be as computationally tractable as the widely used multireference configuration interaction (MR–CI) method. However, because UCEPA is based on a nonvariational energy functional, its energies do not provide upper bounds to the true energies.

In this Note, it is demonstrated how one can obtain a rigorous upper-bound energy E_B with essentially no additional computational effort beyond that needed to perform the UCEPA calculation. To carry out the derivation of this upper bound, we begin with the UCEPA energy functional given in Eq. (2.4) of Ref. 1:

$$E = E_0(1 - \Sigma_n \tau_n^2) + 2\Sigma_n \tau_n \langle 0|H|n\rangle + \Sigma_{n,m} \tau_n \tau_m \langle n|H|m\rangle. \quad (1)$$

Here $|0\rangle$ denotes the (multiconfigurational) reference wave function,

$$|0\rangle = \Sigma_l C_l |l\rangle \quad (2)$$

expressed in terms of a set of M spin and spatial symmetry adapted configuration state functions $\{|l\rangle\}$. The energy E_0 is the expectation value of this reference function $\langle 0|H|0\rangle = E_0$. The functions $\{|n\rangle\}$ contain (i) the so-called orthogonal complement functions to $|0\rangle$; that is, combinations of the same configuration state functions $\{|l\rangle\}$ used to form $|0\rangle$ that are orthonormal and orthogonal to $|0\rangle$, and (ii) a set of orthonormal configuration state functions that lie outside the $\{|l\rangle\}$ space; this set may, for example, consist of configurations that are singly or doubly excited relative to some or all of the $\{|l\rangle\}$ functions. The $\{\tau_n\}$ are amplitudes that describe the UCEPA wave function

$$|\psi\rangle = \exp[\Sigma_n \tau_n (|n\rangle\langle 0| - |0\rangle\langle n|)]|0\rangle \quad (3)$$

in terms of the unitary operator $\exp[\Sigma_n \tau_n (|n\rangle\langle 0| - |0\rangle\langle n|)]$ acting on the reference wave function $|0\rangle$. The matrix elements of the electronic Hamiltonian H among the $\{|0\rangle, |n\rangle\}$ space are denoted $\langle n|H|m\rangle$ and $\langle 0|H|n\rangle$.

The UCEPA energy functional of Eq. (1) is obtained by expanding $\langle\psi|H|\psi\rangle$, with ψ given as in Eq. (3), in powers of the τ_n amplitudes[2] and keeping terms through second order. This power series expansion and subsequent truncation makes the UCEPA energy functional no longer an exact expectation value, and thus no longer an upper bound. However, as proven in the Appendix of Ref. 1, this quadratic truncation is precisely what permits the UCEPA energy to be size extensive.

The equations that determine the optimal $\{\tau_n\}$ parameters within the UCEPA model are obtained by making the UCEPA energy functional stationary. Following Ref. 1, this results in a set of equations that must be solved for the $\{\tau_n\}$:

$$-\langle 0|H|n\rangle = \Sigma_m (\langle n|H|m\rangle - E_0\delta_{n,m})\tau_m. \quad (4)$$

For $\{\tau_n\}$ amplitudes that obey Eq. (4), the UCEPA energy functional of Eq. (1) reduces to (see Ref. 1 for details):

$$E = E_0 + \Sigma_n \tau_n \langle 0|H|n\rangle. \quad (5)$$

It is possible, using the full unitary exponential form of $|\psi\rangle$ given above in Eq. (3), to evaluate the Hamiltonian expectation value of $|\psi\rangle$ without carrying out the second-order truncation that lead to the UCEPA energy functional. As given in Eq. (2.3) of Ref. 1, this yields the following upper-bound energy expression:

$$E_B = E_0 \cos^2 x + 2\frac{\cos x \sin x}{x}\Sigma_n \tau_n \langle 0|H|n\rangle + \frac{\sin^2 x}{x^2}\Sigma_{n,m}\tau_n\tau_m\langle n|H|m\rangle, \quad (6)$$

where the variable x is defined in terms of the $\{\tau_n\}$ by $x^2 = \Sigma_n \tau_n^2$. Using the fact that the $\{\tau_n\}$ amplitudes obey Eq. (4), this upper bund energy can be rewritten as

$$E_B = E_0 + \left(2\frac{\sin x \cos x}{x} - \frac{\sin^2 x}{x^2}\right)\Sigma_n \langle 0|H|n\rangle\tau_n. \quad (7)$$

Comparing Eqs. (7) and (5), it is straightforward to express E_B in terms of E_0, x and the UCEPA energy E:

$$E_B = E_0 + (E - E_0)\left(2\frac{\sin x \cos x}{x} - \frac{\sin^2 x}{x^2}\right). \quad (8)$$

This final result provides a *rigorous upper bound* energy E_B in terms of the reference energy E_0, the UCEPA energy E, and the quantity x that is given in terms of the UCEPA parameters $\{\tau_n\}$ as above; only trivial calculations beyond those needed to perform the UCEPA calculation are needed to evaluate E_B. Having both[3] a size-extensive energy E and an upper bound energy E_B can be of great use to workers implementing the UCEPA technique.

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[1] M. R. Hoffmann and J. Simons, J. Chem. Phys. **90**, 3671 (1989).

[2] These amplitudes are assumed to be small because the reference function $|0\rangle$ is assumed to have been constructed to contain the dominant terms of the wave function.

[3] It should be stressed that the UCEPA energy E is size-extensive but not an upper bound, and E_B is an upper bound but not size-extensive. Of course, it would be wonderful to use methods with one energy that is both size-extensive and variational, but such approaches are thus far limited to methods based on complete-active-space (CAS) configuration lists.

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