Some Comments on the Davidson Correction

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My thesis [1] already discusses the size extensivity problem of truncated configuration interaction methods. Here I will derive the famous Davison correction [2]; my approach follows that of Meissner [3], filling in some of the details. An alternative derivation is also found in Szabo and Ostlund [4]. Additionally, Duch and Diercksen provide a very nice review of size extensivity corrections.

Consider the CID method for m identical noninteracting two-electron systems. Since they are noninteracting, we will write the total wavefunction as a product of wavefunctions for the individual monomers (cf. Szabo and Ostlund, [4] p. 269). The ground state wavefunction for monomer k will be written as determinant $\Phi_0(k)$, while the doubly-excited wavefunction is $\Phi_D(k)$. (Assume that singles are noninteracting). Hence the total wavefunction is (eq. A1 of Meissner)

$$\Psi = c_0 \prod_{k=1}^{m} \Phi_0(k) + c_D m^{-1/2} \sum_{k=1}^{m} \left(\prod_{l=1, l\neq k}^{m} \Phi_0(l) \right) \Phi_D(k), \tag{1}$$

where of course $c_0^2 + c_D^2 = 1$. This approach differs from that of Szabo and Ostlund [4] in that we deal with all the double exitations simultaneously, since they all have the same form and the same coefficient.

Now we diagonalize the Hamiltonian matrix, subtracting out the SCF energy from the diagonal. The determinantal equation is

$$\begin{vmatrix} -E_D & m^{1/2}x \\ m^{1/2}x & y - E_D \end{vmatrix} = 0, \tag{2}$$

where x and y are given by

$$\begin{aligned} x &= m^{-1/2} \langle \prod_{j=1}^{m} \Phi_0(j) | \hat{H} | \sum_{k=1}^{m} \left(\prod_{l=1, l\neq k}^{m} \Phi_0(l) \right) \Phi_D(k) \rangle \\ &= m^{-1/2} \sum_{k=1}^{m} \langle \Phi_0(k) | \hat{H}(k) | \Phi_D(k) \rangle \\ &= m^{1/2} \langle \Phi_0(1) | \hat{H}(1) | \Phi_D(1) \rangle, \end{aligned} \tag{3}$$

and

$$\begin{aligned}
y &= m^{-1}\langle\sum_{i=1}^{m}\left(\prod_{j=1,j\neq i}^{m}\Phi_0(j)\right)\Phi_D(i)|\hat{H}|\sum_{k=1}^{m}\left(\prod_{l=1,k\neq l}^{m}\Phi_0(l)\right)\Phi_D(k)\rangle - E_{SCF}\\
&= m^{-1}\sum_{k=1}^{m}\left[\langle\Phi_D(k)|\hat{H}(k)|\Phi_D(k)\rangle - \sum_{l=1,l\neq k}^{m}\langle\Phi_0(l)|\hat{H}(l)|\Phi_0(l)\rangle\right] - E_{SCF}\\
&= \langle\Phi_D(1)|\hat{H}(1)|\Phi_D(1)\rangle + (m-1)\langle\Phi_0(1)|\hat{H}(1)|\Phi_0(1)\rangle - m\langle\Phi_0(1)|\hat{H}(1)|\Phi_0(1)\rangle\\
&= \langle\Phi_D(1)|\hat{H}(1)|\Phi_D(1)\rangle - \langle\Phi_0(1)|\hat{H}(1)|\Phi_0(1)\rangle. \qquad (4)
\end{aligned}$$

The secular equation yields

$$E_D = -\frac{1}{2}y\left[\left(1+4m\frac{x^2}{y^2}\right)^{1/2}-1\right], \qquad (5)$$

and from the eigenvalue equation,

$$E_D = m^{1/2}x\frac{c_D}{c_0}. \qquad (6)$$

It is reasonable to expect $x << y$. In that case, one can employ the expansion

$$\left(1+4m\frac{x^2}{y^2}\right)^{1/2} = 1+2m\frac{x^2}{y^2}-2m^2\frac{x^4}{y^4}+\cdots \qquad (7)$$

Stopping at three terms, we obtain

$$E_D = -m\frac{x^2}{y^2}+m^2\frac{x^4}{y^3}. \qquad (8)$$

Now recall that the correlation energy should be proportional to the number of monomers in the system, m. The first term is proportional to m and Meissner points out that it is in fact the L-CPMET energy [3]. The second term is instead proportional to m^2 and is responsible (along with the neglected higher-order terms) for the lack of size extensivity. We wish our correction factor to cancel this term. If the first term in eq. (8) is dominant then

$$E_D \approx -m\frac{x^2}{y}. \qquad (9)$$

Combining this equation with eq. (6) yields

$$\begin{aligned}
m^{1/2}x\frac{c_D}{c_0} &\approx -m\frac{x^2}{y}\\
\frac{c_D}{c_0} &\approx -m^{1/2}\frac{x}{y}\\
\frac{1-c_0^2}{c_0^2} &\approx m\frac{x^2}{y^2}. \qquad (10)
\end{aligned}$$

We need to cancel the term m^2x^4/y^3, and we have an expression for mx^2/y^2; hence we need to multiply by $-mx^2/y$, which is approximately E_D! Our correction is thus

$$\Delta = \frac{1 - c_0^2}{c_0^2} E_D, \tag{11}$$

which is the "renormalized" Davidson correction. If $c_0^2 \approx 1$, this is very close to the traditional Davidson correction,

$$\Delta = (1 - c_0^2) E_D. \tag{12}$$

References

[1] C. D. Sherrill, *Computational Algorithms for Large-Scale Full and Multi-Reference Configuration Interaction Wavefunctions*, PhD thesis, University of Georgia, Athens, GA, 1996.

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[3] L. Meissner, Chem. Phys. Lett. **146**, 204 (1988).

[4] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory.* McGraw-Hill, New York, 1989.