

Size Extensivity Correction for Complete Active Space Multiconfiguration Self-Consistent-Field Configuration Interaction Energies

Jack Simons

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112 (Received: June 28, 1988; In Final Form: October 19, 1988)

We present a derivation of an analytical expression that can be used to "correct" configuration interaction (CI) energies for their adherent size inconsistency flaws. This derivation uses CI wave function amplitudes in a size extensive energy functional to achieve its result. This result provides justification for size extensivity correction formulas that have empirically been shown by others to be of use in practical calculations.

Introduction

Truncated configuration interaction (CI) calculations are known¹ to yield total electronic energies that do not scale properly with the number of electrons in the system. This so called "size extensivity" (SE) problem causes truncated CI energies (e.g., those that include all excitations up through some specified level) to be of questionable value, for example, in computing thermodynamic energy differences such as chemical reaction energies. Specifically, for the reaction



truncated-CI energies of the individual species (C, D, A, and B) can *not* be used to evaluate ΔE ; one must evaluate, within the truncated-CI method, the energy of the C + D and A + B "supermolecules" at large C-D and A-B separations and then subtract these two energies to evaluate ΔE .

The SE difficulties are, of course, well-known and well-documented.^{2a} Although it may seem logical to abandon the CI technique because of this flaw, it is, in our opinion, wiser to seek a correction to the conventional CI energy that allows one to maintain the highly developed computational power of the CI method. It is with this attitude that the present work is offered.

In particular, we *assume* that a CI calculation has been carried out according to the following scheme:

(1) A complete active space^{2b} (CAS) CI calculation (or MCSCF if orbital optimization is included) is performed to obtain the CAS-CI function $|\phi\rangle = \sum_I C_I^0 |I\rangle$ in terms of the CAS configuration state functions (CSFs) $\{|I\rangle; I = 1, \dots, M\}$ and a CAS energy $E^0 = \langle \phi | H | \phi \rangle$.

(2) A set of CSFs (denoted $\{|e\rangle\}$) are formed by taking *all*³ excitations out of the CSFs $\{|I\rangle\}$ that constitute $|\phi\rangle$, up through some specified level of excitations. For example, one typically forms all singly and doubly excited CSFs relative to the $\{|I\rangle\}$.

(3) A new larger CI calculation is performed, probably by using "direct" methods,⁴ within the space spanned by the $\{|I\rangle$ and $\{|e\rangle\}$ CSFs to obtain an energy E_{CI} and wave function $|\Psi\rangle = \sum_I C_I |I\rangle + \sum_e C_e |e\rangle$.

The CAS-CI or CAS-MCSCF energy is known to *not* suffer from the SE problem, whereas the above E_{CI} does. We therefore seek to obtain a useful correction to E_{CI} that removes the "SE-causing" factors. The strategy we take involves developing a SE energy functional F , which contains the same matrix elements as one needs to perform the above CAS-CI and "larger" CI calculations and then using the CI expansion coefficients $\{C_I, C_e\}$

in this energy functional to achieve a SE energy estimate. The difference between $F(C_I, C_e)$ and E_{CI} is then viewed as a correction to E_{CI} .

SE Energy Functional

We introduce an exponential unitary operator⁵ $\exp(T)$ to map $|\phi\rangle$ into a trial wave function:

$$|\psi\rangle = \exp(T)|\phi\rangle \quad (2)$$

and express T in terms of a set of amplitudes $\{t_n, t_e\}$ and antiunitary operators:

$$T = \sum_n t_n [|n\rangle\langle\phi| - |\phi\rangle\langle n|] + \sum_e t_e [|e\rangle\langle\phi| - |\phi\rangle\langle e|] \quad (3)$$

Here, the functions $\{|n\rangle\}$ constitute the orthogonal complement of $|\phi\rangle$; they are linear combinations of the CSFs $\{|I\rangle\}$ and are orthogonal to $|\phi\rangle$:

$$|n\rangle = \sum_I C_I^n |I\rangle, \quad n = 1, \dots, M-1 \quad (4)$$

If a CAS MCSCF calculation had been performed to obtain $|\phi\rangle$, then the matrix elements $\langle n | H | \phi \rangle \equiv H_{n\phi}$ vanish according to the generalized Brillouin theorem (GBT). This fact is not used in the further development but is mentioned here to clarify.

The energy functional

$$F \equiv \langle \phi | \exp(-T) H \exp(T) | \phi \rangle \quad (5)$$

is known⁵ to contain only size extensive factors if the $\{|e\rangle\}$ are chosen as described above. Because, by assumption, the *dominant* contributions to $|\phi\rangle$ are contained in $|\phi\rangle$, the optimal t_n and t_e amplitudes are "small". As a result, an expansion of $\exp(-T) H \exp(T)$ in powers of the t amplitudes should be rapidly convergent. Thus we choose to approximate F by its low-order expansion (truncating the expansion certainly destroys the upper bound property^{3a} of F but maintains^{5b} its SE):

$$F \approx F_2 \equiv \langle \phi | H | \phi \rangle + \langle \phi | [H, T] | \phi \rangle + \frac{1}{2} \langle \phi | [[H, T], T] | \phi \rangle \quad (6)$$

Truncation at second order is chosen because doing so allows us to express F in terms of the *same* matrix elements as appear in the "larger" CI calculations. By inserting eq 3 for T into eq 6, we obtain the working equation for F :

$$F_2 = E^0 (1 - \sum_a t_a^2) + \sum_a H_{0a} t_a + \sum_{a,b} t_b H_{ba} t_a \quad (7)$$

where the indexes a and b run over all n and all e .

Evaluation of F_2 in Terms of the CI Wave Function

Our strategy is to use the CI eigenvector $\{C_I, C_e\}$ to *define* a set of $\{t_a\}$ amplitudes to use in eq 7 for evaluating F_2 . This particular set of $\{t_a\}$ amplitudes is, of course, neither the set that makes F stationary *nor* the set that makes the projection of $[\exp(-T) H$

(1) Bartlett, R. J. *Ann. Rev. Phys. Chem.* **1981**, *32*, 359.
 (2) (a) Shavitt, I. In *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules*; Dykstra, C. E., Ed.; Reidel: Dordrecht, 1984, p 185. (b) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157.
 (3) Hoffmann, M. R.; Simons, J. *J. Chem. Phys.* **1988**, *88*, 993; *Chem. Phys. Lett.* **1987**, *142*, 451. The excitations may further be restricted to exclude certain (e.g., core and high-energy virtual) orbitals if desired. Multireference-based CI methods are treated, for example, in the following: Buenker, R. J.; Peyerimhoff, S. D.; Butscher, W. *Mol. Phys.* **1978**, *35*, 771.
 (4) Saunders, V. R.; Van Lenthe, J. H. *Mol. Phys.* **1983**, *48*, 923.

(5) (a) Hoffmann, M. R.; Simons, J. *Chem. Phys. Lett.* **1987**, *142*, 451; *J. Chem. Phys.* **1988**, *88*, 993. (b) Yaris, R. *J. Chem. Phys.* **1964**, *41*, 2419; **1965**, *42*, 3019.

$\exp(T - E)|o\rangle$ along the $\{|a\rangle\}$ vanish. Nevertheless, the F functional yields a SE energy *regardless* of what $\{t_a\}$ amplitudes are used. We therefore define the amplitudes corresponding to the $\{|n\rangle\}$ and $\{|e\rangle\}$ spaces as follows:

$$t_e = C_e/C_o \quad (8a)$$

$$t_n = C_n/C_o, \quad n = 1, \dots, M-1 \quad (8b)$$

where

$$C_o \equiv \sum_I C_I C_I^\dagger \quad (8c)$$

$$C_n \equiv \sum_I C_I C_I^\dagger \quad (8d)$$

are obtained by "transforming" the CI coefficient vector $\{C_I\}$ from the CSF basis $\{|I\rangle\}$ to the $\{|o\rangle, |n\rangle\}$ basis

$$|\Psi\rangle = \sum_I C_I |I\rangle + \sum_e C_e |e\rangle = \sum_n C_n |n\rangle + C_o |o\rangle + \sum_e C_e |e\rangle \quad (9)$$

Given the set of $\{t_n, t_e\} \equiv \{t_a\}$ amplitudes defined in eq 8, the F_2 functional of eq 7 can be evaluated. By making use of the fact that $\{C_o, C_n, \text{ and } C_e\}$ obey the CI eigenvalue equations

$$E_o C_o + \sum_n H_{on} C_n + \sum_e H_{oe} C_e = E_{CI} C_o \quad (10a)$$

$$H_{ao} C_o + \sum_n H_{an} C_n + \sum_e H_{ae} C_e = E_{CI} C_a \quad (10b)$$

for $\{a\} = \{m, e\}$, the expression for F_2 can be rearranged to yield

$$F_2(\{C_I\}) = E^0(1 - \sum_a C_a^2/C_o^2) + E_{CI}(1 + \sum_a C_a^2/C_o^2) - E^0 \quad (11a)$$

$$\begin{aligned} &= E_{CI}(1 + \sum_a C_a^2/C_o^2) - E^0 \sum_a C_a^2/C_o^2 \\ &= E_{CI} + (E_{CI} - E^0) \left(\frac{1 - C_o^2}{C_o^2} \right) \end{aligned} \quad (11b)$$

Using the fact that $C_o^2 + \sum_a C_a^2 = 1$, we then obtain

$$F_2 = E^0 + (E_{CI} - E^0)/C_o^2 \quad (12)$$

Equation 12 expresses a SE energy in terms of the SE E^0 (recall that, by assumption, $|o\rangle$ is a CAS-type wave function) and the

CI correlation energy ($E_{CI} - E^0$) above that contained in E^0 . Recall that C_o , the expansion coefficient of $|o\rangle$ in the CI wave function $|\psi\rangle$, is evaluated as in eq 8d in terms of the CSF-space CI vector $\{C_I\}$ and the CAS function's CSF amplitudes $\{C_I^\dagger\}$. Alternatively, eq 11b expresses the SE energy as the "larger" CI energy E_{CI} plus a correction equal to the correlation energy ($E_{CI} - E^0$) above E^0 multiplied by the ratio $(1 - C_o^2)/C_o^2$.

Discussion

The results given in eq 11b and 12 provide a SE estimate (because we truncated the expansion of F at the F_2 level) of the total electronic energy in terms of the SE reference energy E^0 , the correlation energy above E^0 , ($E_{CI} - E^0$), and C_o^2 , which is the square of the overlap of ψ and $|o\rangle$. This quite simple expression can be viewed as a generalization of the well-known "Davidson correction" which applies to CI calculations based on single-configuration reference functions. The expression given in eq 12 agrees, in form, with that put forth on semiempirical grounds by Brown and Truhlar⁷ and may even be viewed as a justification for the procedure, which they showed is capable of yielding excellent results. When written as in eq 11b, it is of the form used by Feller and Davidson⁸ and by Bauschlicher and Taylor.⁹ It is also similar in spirit to the result of Prime et al.¹⁰ It is applicable only when the truncation of the expansion of F at the F_2 level is accurate; this will be the case whenever the $\{t_a\}$ amplitudes are small. It does *not* give the "best" SE energy estimate within the $\{|I\rangle, |e\rangle\}$ CSF space because the $\{t_a\}$ amplitudes employed do *not* cause $\exp(-T) H \exp(t)|o\rangle = E|o\rangle$ to be obeyed in any optimal sense.

Acknowledgment. The financial support of the National Science Foundation (CHE-8511307) is gratefully acknowledged.

(6) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61; *J. Chem. Phys.* **1976**, *64*, 4699.

(7) Brown, F. B.; Truhlar, D. G. *Chem. Phys. Lett.* **1985**, *117*, 307. These authors introduced a parameter F through $E = E^0 + (E_{CI} - E^0)/F$ and used empirical means to evaluate F .

(8) Feller, D.; Davidson, E. R. *J. Chem. Phys.* **1985**, *82*, 4135. These authors used the functional form $E = E_{CI} + (E_{CI} - E^0)(1 - C_o^2)$ in their studies of electronic affinities of C and O.

(9) Bauschlicher, C. W.; Taylor, P. R. *J. Chem. Phys.* **1986**, *85*, 6510. They also used $E = E_{CI} + (E_{CI} - E^0)(1 - C_o^2)$ in their study of the singlet-triplet splitting in CH_2 .

(10) Prime, S.; Rees, C.; Robb, M. A. *Mol. Phys.* **1981**, *44*, 173.

Polarizability Anisotropy, Magnetic Anisotropy, and Quadrupole Moment of Cyclohexane

Ian E. Craven,^{1a} Mark R. Hesling,^{1a} Derek R. Laver,^{1b} Philip B. Lukins,^{1b} Geoffrey L. D. Ritchie,^{*,1a} and Julian Vrbancich^{1b}

Department of Chemistry, University of New England, New South Wales 2351, Australia, and School of Chemistry, University of Sydney, New South Wales 2006, Australia (Received: May 13, 1988)

Measurements of the Rayleigh depolarization ratio of cyclohexane vapor at 441.6 nm, with rigorous exclusion of the spurious contribution from vibrational Raman scattering, are reported and analyzed to provide a reliable value of the polarizability anisotropy ($10^{40} \Delta\alpha/C \text{ m}^2 \text{ V}^{-1} = -1.93 \pm 0.03$) of this molecule. In addition, observations of the magnetic birefringence of the vapor and the field gradient birefringence of the liquid are interpreted in conjunction with the polarizability anisotropy to yield the magnetic anisotropy ($10^{29} \Delta\chi/J \text{ T}^{-2} = 19.2 \pm 2.4$) and the quadrupole moment ($10^{40} \Theta/C \text{ m}^2 = 3.0 \pm 1.0$) of cyclohexane. The anisotropy in the second moment of the electronic charge distribution and other fundamental electric and magnetic properties of cyclohexane are also evaluated and discussed.

Introduction

Reliable measurements of fundamental electric and magnetic characteristics of small molecules such as cyclopropane² and

cyclohexane are currently of interest. The Rayleigh depolarization ratio of a gas provides information as to the anisotropy in the molecular polarizability, one of the most important of these

(1) (a) University of New England. (b) University of Sydney.

(2) Lukins, P. B.; Laver, D. R.; Buckingham, A. D.; Ritchie, G. L. D. *J. Phys. Chem.* **1985**, *89*, 1309-1312.