Including dispersion in configuration interaction-singles calculations for the spectroscopy of chromophores in solution

Sylvio Canuto,^{a)} Kaline Coutinho,^{b)} and Michael C. Zerner *Quantum Theory Project, University of Florida, Gainesville, Florida* 32611

(Received 13 May 1999; accepted 4 February 2000)

In this paper we prove that a configuration interaction electronic structure calculation on a supermolecule that contains only single excitations includes dispersion interactions between the two subsystems when energy differences are taken between the Hartree–Fock (molecular orbital) ground state and low energy excited states in which single excitations dominate. This theorem is proven up to second order in perturbation theory. © 2000 American Institute of Physics. [S0021-9606(00)51816-9]

INTRODUCTION

It is well known that configuration interaction calculations that include only single excitations from a Hartree-Fock ground state reference (CIS) often accurately produce the nature of the low-lying states of molecular systems. Although this procedure does not always yield accurate predictions of transition energies using *ab initio* methods,¹ this observation is at the heart of such parametrized models as the Pariser-Parr-Pople model² and the intermediate neglect of differential overlap model for spectroscopy.³ Most often these models are parametrized at the CIS level of theory, and it is assumed that such a procedure includes the essential correlation directly through the CI and dynamic correlation is built in through the use of semiempirically derived parameters.⁴ CIS has several advantages. It is first of all simple. Most low lying excited states are, as mentioned, dominated by single excitations. And CIS is a size extensive theory-that is, the results are not expected to get worse as the system size increases. This latter feature is important in the context of this work, as we are eventually interested in calculating the spectroscopy of molecules (solutes or chromophores) in solvents. This is the usual case met in every day laboratory chemistry.

The spectroscopy of molecules that are dissolved in solvents can undergo sizable energy shifts.⁵ Since most spectroscopy is taken of chromophores in solution, it is quite important to understand these shifts and to develop methods for estimating them. These shifts can stem from several sources. The largest of these are believed to be caused by the differences in the electrostatic interactions between the moments of a solute in its ground state and its excited state with the induced moments of the solvent.⁶ A second large effect, usually causing a redshift between the gas phase absorption maxima and the solution situation, is due to the differing stabilization of the ground state and the excited state due to dispersion-interactions between the induced moments of the

^{a)}Permanent address: Instituto de Fisica, Universidade de Sao Paulo, CP 66318, 05315-970 Sao Paulo, SP, Brazil; electronic mail: canuto@if.usp.br ^{b)}Permanent address: Universidade de Mogi das Cruzes/CCET, CP 411, solute and solvent.^{7–9} For a nonpolar solute molecule the major shifts are caused by dispersion. Other effects are also active. For example, for small molecules where there are low lying Rydberg states, these states are shifted to much higher energy because of the interaction of these larger states directly with the small cavity which the molecule has created in the solvent for its much smaller ground state. Creating a large cavity costs energy.

Here we examine the differential dispersion between the excited chromophore and the solvent and the ground state of the chromophore and the solvent that are the major causes of the redshift in nonpolar solvents. In this work we prove a remarkable theorem. In a supermolecule calculation including solute and solvent, the differences in energies between the ground state, described by a Hartree-Fock wave function, and a state that is dominated by single excitations includes the dispersion through second order in perturbation theory even though the calculation is of the singles only type. That is, the double excitations that lead to the dispersion energy in the ground state, those confined to single promotions on the chromophore and single promotions on the interacting solvent molecule, see Fig. 1, panel (i), and the special triple excitations that are required to disperse the excited state, confined to single excitations on the chromophore relative to the single excitations dominating the excited state description coupled with single excitations on the solvent, Fig. 1, panel (j), exactly cancel. In the supermolecule calculation the dispersion shifts in the energy differences are generated through the CI matrix elements between the singles localized on the solute and those localized on the solvent, Fig. 2, panel (a). This does not infer that either the ground state or the excited state includes the dispersion. This is not true in a CIS calculation, and is discussed in some detail in Ref. 9.

Dispersion is generally assigned to the electrostatic interactions between molecules that remain after all contributions from permanent moments have been removed.^{6(a)} When the chromophore has a permanent dipole, differences between ground and excited state dipole moments are expected to dominate in the description of spectroscopic shifts.⁶ An example where dispersion is the leading term in causing the

7293

⁰⁸⁷⁰¹⁻⁹⁷⁰ Mogi das Cruzes, SP, Brazil.



FIG. 1. Characterization of some of the excited state wave functions in a supermolecule system containing two molecules c and s. Panels (f) and (g) represent only two of the four types of doubles that can correlate the ground state, see the text. Panel (h) represents only one of very many possible charge transfer doubles. Panel (j) is the only triple excitation to be considered, as it "disperses" the excited state $i \rightarrow a$.

spectroscopic shift is benzene in cyclohexane. The first nonvanishing moment of benzene is the quadrupole, and the difference between the ground and first excited state quadrupole is very small. This contribution to the shift in the spectra of benzene in cyclohexane and benzene in the gas phase has been estimated as $+15 \text{ cm}^{-1}$. The observed redshift is -300 cm^{-1} , and the difference is believed caused by dispersion.^{8,9}

In Fig. 1 we catalog the excitations that arise in a configuration interaction treatment, assuming a ground state closed-shell reference. Single excitations, panel (b), localized on the solute, labeled c for chromophore, are assumed to dominate in the description of the low lying spectrum. Single excitations on the solvent, labeled s, are assumed at higher energy, or else this would be a poor choice of solvent. Interactions through a CIS of these two types of localized single excitations in a CIS treatment give rise to excitonic coupling, Fig. 2 panel (a). Excitations of the charge transfer type are generally at higher energy, estimated as electron affinities minus ionization potential minus $1/R_{cs}$, where R_{cs} is the average distance between c and s in atomic units. Their presence at low energies is rather unusual and rather dramatic, often leading to colored solutions from colorless components. The double excitations of panel (f) correlate to the ground state of the chromophore, and those of panel (g) correlate to the solvent ground state. The double excitations of panel (h) represent some of the many double excitations that are of charge transfer type. The double excitation of panel (i) represents those that lead to the dispersion of the ground state, that "disperse" the ground state (here we introduce a



FIG. 2. Superposition of singles resulting from the diagonalization of the A matrix, see the text.

verb for later convenience). The interactions that disperse the single excited states that result from a CIS treatment of the chromophore are triple excitations with respect to the reference Hartree–Fock ground state, and they are shown in panel (j).

In general, the wave function of a composite system of N total electrons can be written as

$$\Psi_{I'J'}(1,...,N) = \sum_{p} \sum_{I} \sum_{J} \mathsf{A}[\psi_{I}^{A}(1,...,p)\psi_{J}^{B}(p+1,...,N)].$$

We define two subsystems A and B in a system containing A and B as "separate" if we can ignore the exchange integrals between them. In the above wave function this suggests that the antisymmetrizer A between the A and B subsystems can be ignored. This implies, in turn, that the molecular orbitals (mo's) of the composite system are localized on A or B, or the exchange integrals would not, in general, vanish. Since each orbital has integral occupation, 2, 1, or 0, and is local, then each subsystem, in turn, has an integer number of electrons, say p' in system A. Then

$$\Psi_{I'J'}(1,...,N) = \sum_{I} \sum_{J} \psi_{I}^{A}(1,...,p') \psi_{J}^{B}(p'+1,...,N).$$

This is clearly generalizable to a collection of many weakly interacting subsystems.

Note that the above-mentioned "separation" does not imply that each subsystem need be neutral, nor that the interaction need be weak (considered charges species), but just that the wave function can be written as the sum of simple products with a fixed number of electrons. In addition, a subsystem can be sizably perturbed by the presence of other subsystems, accommodated in the above wave function since all states of the unperturbed subsystems are included in the sums. This separation is the basis for the perturbation theory treatment of two separate systems and of dispersion.

THEOREM

The differences in energy calculated in self-consistent field (SCF)-CIS treatment on a supermolecule consisting of two weakly interacting molecules is equivalent to a CI treatment including the doubles and triples that disperse the reference ground state and all singly excited states, respectively, through second order in Møller–Plesset perturbation theory.

In Møller–Plesset perturbation theory the zeroth-order energy is the sum of the occupied orbitals, and $H^0 = \sum_i f(i)$, with f(i) the Fock operator for orbital ϕ_i , and the zeroth- plus first-order correction is the SCF energy; i.e., the expectation value of a single determinant in the typical closed-shell case.⁹ The Fock operator $f(i) = h(i) + \nu(i)$ and the perturbation is $V = -\sum \nu(i) + \sum_{i < j} 1/r_{ij}$.

A CIS treatment includes the excitations shown in panels (b)-(e), and their interactions shown in Fig. 2, by definition. The only assumption we need to make for this theorem is that the exchange integrals between the two separate molecules vanish. We will show later in the discussion that even most of these exchange integrals will cancel, but not all.

The examination of such a theorem is motivated by the successes we have recently had in examining the spectroscopic shifts of nonpolar chromophores in nonpolar media using single only methods.^{10,11}

PROOF

There are several ways to begin this proof, but the following likely demonstrates best what exactly is being proven, and the conditions on the proof. As discussed in the following, it is not necessarily the easiest way to prove this.

Consider a closed-shell ground state of a two-component supermolecule, A (perhaps the chromophore c) and B (perhaps the solvent s). Assume that the molecular orbitals obtained from the SCF are principally localized on A or B, or can be made so. Consider a CI that consists of all singles, the doubles that disperse the ground state, panel (i) of Fig. 1, and all triples that disperse all the single excitations, panel (j) of Fig. 1. The CI does not contain the localized double excitations that would correlate the ground state of A, panel (f) of Fig. 1 [there are four classes of such doubles, only one of which is shown in this panel: $(i,i) \rightarrow (a,a), (i,i) \rightarrow (a,b),$ $(i,j) \rightarrow (a,a)$ and two from $(i,j) \rightarrow (a,b)$, with ϕ_i and ϕ_i occupied molecular orbitals of A and ϕ_a and ϕ_b virtual orbitals of A], or those similar double excitations localized on B, panel (g) of Fig. 1, with mo labels k and c assigned to orbitals localized on B. Although the inclusion of such doubles certainly improves the description of the ground state of the system, they unbalance the CI for the purposes of calculating spectroscopy by lowering the ground state energy far more than most of the singly excited configurations that are the principle components of the low lying excited states. The charge resonance doubles are also not included, panel (h) of Fig. 1, nor are the charge transfer doubles shown, for they are assumed to lie at much higher energy. The localized triple excitations that would correlate the single excited configurations and restore the balance to the CI for the calculation of spectroscopy if the correlating doubles were included, are likewise not included. A CISDT of this nature is known to yield good spectroscopic predictions, but is a sizable calculation. (This model, of course, is not necessarily a good predictor of two-photon states, i.e., those that are dominated by double excitations might need to be correlated by quadruples, etc.) In the following we consider diagonalizing the space of all singles, the so-called A matrix, and include all the other states, those that disperse both the ground state and all singles, through second order in Møller-Plesset perturbation theory.

We write

$$\Psi_0 = \psi_0^A \psi_0^B = |1\,\overline{1}\cdots i\,\overline{i}\cdots j\,\overline{j}\cdots k\,\overline{k}\cdots|.$$
(1)

Although we write the ground state wave function as a product of the two pieces, this is only to suggest where the excitations will be localized. The wave function as written on the right-hand side is an exact representation of the Hartree– Fock reference. |...| represents the usual Slater determinant, and a bar over an orbital designates beta spin.

Single excitations are written as

$$\psi_{ia}^{A}\psi_{0}^{B} = (ia) \equiv [|1\bar{1}\cdots i\bar{a}\cdots j\bar{j}\cdots| + |1\bar{1}\cdots a\bar{i}\cdots j\bar{j}\cdots|]/\sqrt{2}, \qquad (2)$$

where we are using the Rumer diagram construction 12,13 for convenience,

$$\widehat{ia} = (i\overline{a} + a\overline{i})/\sqrt{2} \tag{3}$$

The interaction of two single excitations, required, for example, to complete the CIS A matrix is

$$\langle \psi_{ia}^{A}\psi_{0}^{B}|H|\psi_{jb}^{A}\psi_{0}^{B}\rangle = 2\langle aj|ib\rangle - \langle aj|bi\rangle \tag{4}$$

with

$$\langle aj|ib \rangle = \langle a(1)j(2)|i(1)b(2) \rangle$$

= $\int \partial V(1) \int \partial V(2) \phi_a^*(1) \phi_i(1) r_{12}^{-1} \phi_j^*(2) \phi_b(2).$ (5)

This matrix element is the same for any single with any other single, i.e.,

$$\langle \psi_{ia}^{A}\psi_{0}^{B}|H|\psi_{0}^{A}\psi_{kc}^{B}\rangle = 2\langle ak|ic\rangle - \langle ak|ci\rangle \approx 2\langle ak|ic\rangle.$$
(6)

The approximation in Eq. (6) that sets the exchange terms $\langle ak|ci\rangle = 0$ is the only *operational* approximation that we will make in the following, and is the condition stated on the theorem. We will come back to this approximation, for if not made it suggests correction terms of a rather simple nature. If the molecular orbitals of the two subsystems are reasonably well localized this exchange will be small. If these orbitals are not localized then these integrals might not be small and the ideas behind treating the two subsystems separately are not valid. The spectroscopic shifts in such a strongly perturbed system may be sizable, and still should be predicted by this treatment, as CIS is a size extensive model, but the interpretation of these terms as in Fig. 1 is not clear.

Double excitations that disperse the ground state are of the form $\psi_{ia}^A \psi_{kc}^B$. There are two singlets that arise from four open shells.

$$\begin{split} \psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{I}) &= (\widehat{jb})(\widehat{kc}) \\ &= 1/2[|\cdots j\overline{b}\cdots k\overline{c}\cdots|+|\cdots j\overline{b}\cdots c\overline{k}\cdots| \\ &+|\cdots b\overline{j}\cdots k\overline{c}\cdots|+|\cdots b\overline{j}\cdots c\overline{k}\cdots|], \end{split}$$
(7a)
$$\psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{II}) &= (\widehat{jc})(\widehat{kb}) \\ &= 1/2[|\cdots j\overline{c}\cdots k\overline{b}\cdots|+|\cdots j\overline{c}\cdots b\overline{k}\cdots| \\ &+|\cdots c\overline{j}\cdots k\overline{b}\cdots|+|\cdots c\overline{j}\cdots b\overline{k}\cdots|]. \end{split}$$
(7b)

The matrix elements of interest are

$$\langle \psi_0^A \psi_0^B | H | \psi_{ib}^A \psi_{kc}^B (\mathbf{I}) \rangle = 2 \langle bc | jk \rangle, \tag{8}$$

$$\langle \psi_0^A \psi_0^B | H | \psi_{jb}^A \psi_{kc}^B (\mathrm{II}) \rangle = -\langle bc | jk \rangle.$$
(9)

The Rumer states $\psi_{jb}^A \psi_{kc}^B(I)$ and $\psi_{jb}^A \psi_{kc}^B(II)$ are not orthogonal,

$$\left\langle \psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{I}) \middle| \psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{II}) \right\rangle = -1/2.$$
(10)

Schmidt orthogonalizing $\psi_{ib}^A \psi_{kc}^B$ (II) to $\psi_{ib}^A \psi_{kc}^B$ (I) yields

$$\psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{II})' = \psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{II}) + 1/2\psi_{jb}^{A}\psi_{kc}^{B}(\mathbf{I})$$
(11)

and

$$\langle \psi_0^A \psi_0^B | H | \psi_{jb}^A \psi_{kc}^B (II)' \rangle = 0.$$
 (12)

Using Møller–Plesset perturbation theory for the depression of the ground state yields the familiar second-order equation

$$E_0(\text{disp}) = \sum_{j,b}^{A} \sum_{k,c}^{B} 4\langle bc | jk \rangle^2 / (\epsilon_j + \epsilon_k - \epsilon_b - \epsilon_c), \quad (13)$$

which has been used to estimate dispersion many times.⁸ In this equation, the symbols A and B above the sums is meant to restrict the lower indices to mo's centered on A or on B (or c and s in Fig. 1). This expression can be derived directly considering the six possibly $S_z=0$ determinants that arise from four open-shell orbitals interacting with $\psi_0^A \psi_0^B$, that is, from standard diagrammatic perturbation theory.

Examining now the terms that disperse the singly excited state ψ_{ia}^A yields states of the form $\psi_{ijab}^A \psi_{kc}^B$, panel (j) of Fig. 1. This represents six open shells, from which can be constructed five singlets. The state

$$\psi^{A}_{ijab}\psi^{B}_{kc}(\mathbf{I}) = \widetilde{(ia)}\widetilde{(jb)}\widetilde{(kc)}$$
(14)

yields matrix elements that disperse ψ_{ia}^{A} of

$$\langle \psi_{ia}^{A} \psi_{0}^{B} | H | \psi_{iajb}^{A} \psi_{kc}^{B} (\mathbf{I}) \rangle = 2 \langle jk | bc \rangle.$$
(15)

The remaining four singlets that arise are

$$\begin{aligned}
\psi^{A}_{ijab}\psi^{B}_{kc}(\mathrm{II}) &= (\widehat{jb})(\widehat{ka})(\widehat{ic}), \\
\psi^{A}_{ijab}\psi^{B}_{kc}(\mathrm{III}) &= (\widehat{ja})(\widehat{ib})(\widehat{kc}), \\
\psi^{A}_{ijab}\psi^{B}_{kc}(\mathrm{IV}) &= (\widehat{ic})(\widehat{kb})(\widehat{ja}), \\
\psi^{A}_{ijab}\psi^{B}_{kc}(\mathrm{V}) &= (\widehat{ia})(\widehat{jc})(\widehat{kb}),
\end{aligned}$$
(16)

and they all yield a zero matrix element with $\psi_{ia}^A \psi_0^B$ after they have been orthogonalized to $\psi_{ijab}^A \psi_{kc}^B$ (I). The dispersion of the state $\psi_{ia}^A \psi_0^B$ is then given by

$$E_{ia}(\text{disp}) = \sum_{j,b}^{A} \sum_{k,c}^{B} 4\langle bc | jk \rangle^{2} / (\epsilon_{j} + \epsilon_{k} - \epsilon_{b} - \epsilon_{c}).$$
(17)

This is exactly the same as Eq. (13). The possibility that in this sum orbital φ_j might equal φ_i , or orbital φ_b might equal φ_a is discussed in the following. Again, this expression can be derived directly by considering the six $S_z=0$ determinants that can be generated from each of $|1\overline{1}\cdots i\overline{a}\cdots j\overline{j}\cdots k\overline{k}\cdots|$ and $|1\overline{1}\cdots a\overline{i}\cdots j\overline{j}\cdots k\overline{k}\cdots|$ exciting j $\rightarrow b$ and $k \rightarrow c$, and dividing by two [the normalizer squared in Eq. (2)]. In the supermolecule calculation the ground state and each singly excited state would be dispersed by the same amount if these terms were calculated (to second order). The terms that reproduce dispersion arise in the supermolecule calculation in several places. First, all the orbitals of *A*, and thus the resultant integrals that comprise both the SCF and CI are effected by the permanent or induced moments of *B*. Second, terms that shift the spectroscopic states (energy differences) arise in the supermolecule calculation from the CIS matrix elements $\psi_{ia}^A \psi_{kc}^B$ that would not be present in the separate system calculations, but are included automatically in the all singles supermolecule calculation, Fig. 2. Although calculated explicitly in the CIS, they can also be estimated from perturbation theory using Eq.(6),

$$\Delta E_{ia} \approx E_{ia} + E_{ia}(\text{disp}) + E_{ia}(\text{CIS})$$
$$-(E_0 + E_0(\text{disp}) + E_0(\text{CIS})). \tag{18}$$

 $E_0(\text{CIS})=0$ by Brillouin's theorem in the supermolecule calculation. This yields the estimated shift

$$\Delta E_{ia} \approx E_{ia} - E_0 + E_{ia} (\text{CIS}-\text{on}-A) + \left\{ \sum_{k,c}^B 4\langle ic | ak \rangle^2 / (\epsilon_i + \epsilon_k - \epsilon_a - \epsilon_c) \right\}.$$
(19)

The term in brackets is due to terms not present in the two separate calculations.

Equation (19) is only approximate, and is not used. The CIS **A** matrix is diagonalized for the supermolecule. We need only note that the dispersing doubles and triples, if considered, would add a constant to all the diagonal elements of the CIS matrix and not effect energy differences. The absolute energy of each state, and the eigenvectors, of course, are effected.¹⁴

This completes the proof and the provisos around it. No doubt it also helps to explain why simple parametrized CIS calculations can be so successful even for composite systems.^{10,13} It also bodes well for *ab initio* models of correlation that are based on the idea that the single excitations are the important ones for spectroscopy, such as SAC-CI¹⁵ and STEOM.¹⁶ However this analysis also points out that single excitations from heavily correlated reference states, the underlying theme of SAC-CI and STEOM, might not be as successful as heavily correlating the ground and the singly excited states, where advantage of these cancellations can be used.

It may be that this theorem is also true to higher orders in perturbation theory. We have not explored this. However, the above demonstration with its provisos is also true for random phase approximation calculations.^{17–19}

We might examine this theorem further, not neglecting the exchange terms $\langle ak | ci \rangle$, Eq. (6). The ground state dispersion energy is then given by

$$E_{0}(\text{disp}) = \sum_{j,b}^{A} \sum_{k,c}^{B} 4(\langle bc | jk \rangle^{2} + \langle bc | kj \rangle^{2} - \langle bc | jk \rangle$$
$$\times \langle bc | kj \rangle) / (\epsilon_{j} + \epsilon_{k} - \epsilon_{b} - \epsilon_{c}), \qquad (20)$$

Downloaded 29 Jul 2002 to 143.107.133.142. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp



FIG. 3. When a=b (shown) or i=j (not shown), the definition of dispersion becomes less clear. We define this as those states generated from singles from c that do not flip the spin of i, coupled with singles from c, see the text. In such a case the two determinants of the state $\psi_{ia}^A \psi_b^B$ are treated separately. If more than dispersion is included, this would need to be corrected for the actual state as given in Eq. (2). A vertical line, without an arrow up or down, designates the Rumer couple, in this case kc.

which reduces to Eq. (13) setting the exchange to zero. The excited state dispersion, using the above-delineated triply excited states, becomes

$$E_{ia}(\operatorname{disp}) = \sum_{j,b}^{A} \sum_{k,c}^{B} (4\langle bc | jk \rangle^{2} + 4\langle bc | kj \rangle^{2} - 4\langle bc | jk \rangle$$

$$\times \langle bc | kj \rangle) / (\epsilon_{j} + \epsilon_{k} - \epsilon_{b} - \epsilon_{c})$$

$$- \sum_{j}^{A} \sum_{k,c}^{B} 3\langle ac | kj \rangle^{2} / (\epsilon_{j} + \epsilon_{k} - \epsilon_{c} - \epsilon_{c})$$

$$- \sum_{b}^{A} \sum_{k,c}^{B} 3\langle bc | ki \rangle^{2} / (\epsilon_{i} + \epsilon_{k} - \epsilon_{c} - \epsilon_{b})$$

$$+ \sum_{k,c}^{B} 3\langle ac | ki \rangle^{2} / (\epsilon_{i} + \epsilon_{k} - \epsilon_{c} - \epsilon_{a}). \qquad (21)$$

Equations (17) (and 21) include the possibility that j equals i and a equals b. The inclusion of these terms in the first sum are needed to cancel against similar terms in the expression for $E_0(\text{disp})$. Such double excitations as $\psi^A_{ia}\psi^B_0 \rightarrow \psi^A_{iaia}\psi^B_{kc}$ do exist, and they would enter the general treatment of correlation, but whether these are truly dispersive is difficult to ascertain. It seems consistent to include the terms suggested in Fig. 3, which requires considering each of the two possible determinants in $\psi^A_{ia}\psi^B_0$ separately, interacting them with determinants, rather than spin-states, which do not flip the spin of ϕ_i or ϕ_a . Doing so, leads to, for b=a, $i \neq j$,

$$E_{ia}^{a=b,i\neq j}(\text{disp}) = \sum_{j}^{A} \sum_{k,c}^{B} (4\langle ac | jk \rangle^{2} + \langle ac | kj \rangle^{2} - 4\langle ac | jk \rangle \langle ac | kj \rangle)/(\epsilon_{j} + \epsilon_{k} - \epsilon_{c} - \epsilon_{a})$$
(22)

and a similar term for i=j, $a \neq b$ and for the term i=j, a = b. These terms in the sums for $E_{ia}(\text{disp})$ do differ from those in E_0 (disp) by exchange terms of the form neglected, $\langle ac|kj\rangle^2$, and it is not possible to eliminate them by simple rotations of the Rumer states.²⁰ The second, third, and fourth sums on the right-hand side of Eq. (21) correct for the inclusion of these terms in the first sum. Including these integrals for the general case is not difficult, as the integrals in these N^3 sums have already been evaluated for the CIS. However, we are relying on cancellations in the theorem, and have avoided the question of instabilities caused by small denominators and intruder states, that regardless of how poor, should cancel until we actually start adding such terms. We should also note that defining dispersion in the cases separated above is somewhat arbitrary. In a complete CI treatment, these states we have separated out would also need to be proper spin-adapted states, rather than determinants that do not change the spin of ϕ_i or ϕ_a . The correction then is not of the form of Eq. (22), nor could these terms be dubbed "dispersive." The situation is identical to including the Brillouin theorem violating terms in constructing the two doublets that arise, for example, in exciting an electron from a doubly occupied orbital to a virtual orbital based on a SCF ground state doublet reference. One of these three open-shell doublets (at least one) requires a spin-flip of the reference doublet, and is, in this sense, similar to a double excitation, and therefore renders Brilloiun's theorem invalid. Such a matrix element begins to correlate the reference, and these excitations we do not include, by definition, as dispersive.

Equations such as (20) and (21) can be obtained directly from Møller–Plesset perturbation theory, and this has been suggested above, and then the various terms depicted in Fig. 1 separated. This leads to the same results under the same approximations, but the various terms that enter, singles, doubles, triples, are not as clear unless the perturbation sequence is developed diagrammatically.

Before concluding, it might be appropriate to reemphasize that the zeroth-order Hamiltonian used in two separate calculations is different from that used in the supermolecule calculation. The perturbation is then different, and this is what leads to the surprising result that the dispersion is included to some degree in a CIS estimate of energy differences.

The overall electronic Hamiltonian is given by

$$H = \sum_{i} p_{i}^{2} / 2m - \sum_{i} \sum_{C} Z_{C} / R_{i,C} + \sum_{i < j} 1 / r_{ij} + \sum_{C < D} Z_{C} Z_{D} / R_{CD}.$$
 (23)

Downloaded 29 Jul 2002 to 143.107.133.142. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

Neglecting the antisymmetrizer between A and B, i.e.,

$$\Psi_0 = \psi_0^A \psi_0^B = |1\,\overline{1}\cdots\overline{i}\overline{i}\cdots\overline{j}\overline{j}||\cdots k\overline{k}\cdots|$$

[contrast this to Eq. (1)] suggests a Hamiltonian constructed in two pieces

$$H = \sum_{i}^{A} p_{i}^{2}/2m - \sum_{i}^{A} \sum_{C}^{A} Z_{C}/R_{i,C} + \sum_{i < j}^{A} 1/r_{ij} + \sum_{C < D}^{A} Z_{C}Z_{D}/R_{CD} + \sum_{i}^{B} p_{i}^{2}/2m - \sum_{i}^{B} \sum_{C}^{B} Z_{C}/R_{i,C} + \sum_{i < j}^{B} 1/r_{ij} + \sum_{C < D}^{B} Z_{C}Z_{D}/R_{CD} + 1/2 \left\{ -\sum_{i}^{A} \sum_{C}^{B} Z_{C}/R_{i,C} + \sum_{i}^{A} \sum_{j}^{B} 1/r_{ij} + \sum_{D}^{A} \sum_{C}^{B} Z_{C}Z_{D}/R_{CD} \right\} + 1/2 \left\{ -\sum_{i}^{B} \sum_{C}^{A} Z_{C}/R_{i,C} + \sum_{i}^{B} \sum_{j}^{A} 1/r_{ij} + \sum_{D}^{B} \sum_{C}^{A} Z_{C}Z_{D}/R_{CD} \right\},$$

$$(25)$$

$$H \equiv H_A + H_B + H_{AB} + H_{BA}$$

= $(H_A + H_{AB}) + (H_B + H_{BA}) \equiv H'_A + H'_B.$ (26)

The term H_{AB} in H'_A "polarizes" A, and H_{BA} in H'_B "polarizes" B, and this is included naturally in the supermolecule SCF (which does not rely on this division). In the supermolecule calculation, the perturbation contains only the two-electron terms treated above,

$$-\sum_{i} \nu(i) + \sum_{i < j} 1/r_{ij},$$

where $\nu(i)$ is the Fock two-electron potential for electron *i*. The zeroth-order solutions can be considered SCF solutions of H'_A and H'_B . In the separate calculations, the term $(H_{AB} + H_{BA})$ is the perturbation, and the zeroth-order solutions are SCF solutions of H_A and H_B . In comparing the molecular orbitals, we note that those obtained from the supermolecule calculation can be expressed as linear combinations of those obtained for the isolated A system (assuming the mo's are localized). Each simple configuration state function of A in the supermolecule could then be expressed as a linear combination of configuration state functions over the mo's of the isolated A system: that is, in terms of the isolated A mo's each configuration state function (CSF) of A in the supermolecule could when an edge position, the coefficients of which are determined by the supermolecule SCF.

We were first led to believe in the existence of such a theorem as that examined here after noting the successes of a series of CIS calculations performed on a chromophore in solution. In those studies, Monte Carlo calculations were performed to generate uncorrelated structures, and then SCF-CIS supermolecule calculations were performed on the chromophore and its first solvation shell (defined through the radial distribution function). These results are then averaged to give peak widths and positions. Success was obtained even in systems such as benzene in benzene, in cyclohexane, in carbon tetrachloride, and in water, cases in which dispersion dominates.¹¹

It would certainly be interesting to further examine this theorem numerically. The comparison that should be made, however, is between the CIS supermolecule calculation and then the CI supermolecule calculation in which the dispersion is included explicitly for the ground and for the excited state of the chromophore; that is, we should check the approximate theory for dispersion the theorem suggests against the theory correctly implemented. The latter calculation is very difficult,⁹ which is why the theorem is potentially so important, and we are presently writing the code to make such calculations. Such calculations were examined in a somewhat different context in Ref. 9. Dispersing the ground state of the chromophore, say subsystem A, is a selected CID, as discussed above, panel (i) of Fig. 1, and dispersing the single excited states involves selected triples, panel (j) of Fig. 1. The completeness of this straightforward treatment can be measured by calculating the summed oscillator strengths for excitations from the ground state of B and from the ground and excited states of A. According to the Thomas-Reiche-Kuhn sum rule²¹

$$N^{A} = \sum_{k} f^{A}_{IK},$$

$$f^{A}_{IK} = 2/3 [E^{A}_{K} - E^{A}_{I}] \mu^{2}_{KI},$$
(27)

where N^A is the number of electrons on subsystem A (or B), f_{IK}^A is the oscillator strength of the transition from state I to K on A, and μ_{KI} is the transition dipole between states K and I. This relationship holds only for a complete basis and a complete CI. Typically if I is the ground state, $\psi_0^A \psi_0^B$, and A and B are reasonably small molecules, N obtained might account for 50% of the active electrons in the CI.¹⁷ If care is used in selecting the triples, an N^A can be obtained when $I = \psi_{ia}^A \psi_0^B$ similar to that obtained for the ground state, but most often N^A obtained for excitations from $\psi_{ia}^A \psi_0^B$ is considerably smaller than that obtained for the ground state. Proceeding blindly evaluating the sums in the perturbation theory expansion, or even performing a reasonably large CI does not even reproduce the redshift of the first excited state that must result from dispersion.⁷ If corrections are made for the missing states (including the continuum) by using the Thomas-Reiche-Kuhn sum rule for A in its ground and excited states, and for B, results reasonably insensitive to the nature of the CI, or the states included in the sums, can be obtained.⁹ But there is no reason to believe that this estimate of the theory properly implemented is any better than the estimate made in the supermolecule CIS.

ACKNOWLEDGMENTS

This work was supported in part through a grant from the Office of Naval Research, CNPq and FAPESP.

- ¹J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frish, J. Phys. Chem. **96**, 135 (1992).
- ²R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (Benjamin, Boston, 1963).
- ³ (a) J. Ridley and M. C. Zerner, Theor. Chim. Acta **32**, 111 (1973); (b) M. C. Zerner, G. H. Loew, R. F. Kirchner, and U. T. Mueller-Westerhoff, J. Am. Chem. Soc. **102**, 589 (1980); (c) M. C. Zerner, in *Reviews of Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1991), Vol. 1, pp. 313–366.
- ⁴(a) Y. S. Lee and K. F. Freed, J. Chem. Phys. **77**, 1984 (1982); (b) Y. S. Lee, H. Sun, and K. F. Freed, *ibid.* **73**, 1472 (1980); (c) Y. S. Lee and K. F. Freed, *ibid.* **79**, 839 (1983); (d) C. Martin and M. C. Zerner, in *Inorganic Electronic Structure and Spectroscopy*, edited by B. Lever and E. Solomon, (in press).
- ⁵C. Reichardt, *Solvent Effects in Organic Chemistry* (Chemie, Weinheim, 1979).
- ⁶(a) A. T. Amos and B. L. Burrows, Adv. Quantum Chem. 7, 289 (1973);
 (b) E. G. McRae, J. Phys. Chem. 61, 562 (1957); (c) M. M. Karelson and M. C. Zerner, *ibid.* 96, 6949 (1992).
- ⁷W. Liptay, Z. Naturforsch **112**, 9405 (1965).
- ⁸T. Abe, Y. Amako, T. Nishioka, and H. Azumi, Bull. Chem. Soc. Jpn. **39**, 845 (1966).
- ⁹N. Rösch and M. C. Zerner, J. Phys. Chem. 98, 5817 (1994).
- ¹⁰A. Szabo and N. Ostlund, *Modern Quantum Chemistry*, 1st ed. (Macmillian, New York, 1982).

- ¹¹K. Coutinho, S. Canuto, and M. C. Zerner, J. Chem. Phys. (submitted).
- ¹²(a) R. Pauncz, Spin Eigenfunctions (Plenum, New York, 1979); (b) R. Manne and M. C. Zerner, Int. J. Quantum Chem. **19**, 165 (1985).
- ¹³J. McKelvey and M. C. Zerner (unpublished). This is the basis used in the open-shell CI in the program ZINDO by Zerner and co-workers.
- ¹⁴ M. G. Cory, M. C. Zerner, X. H. Hu, and K. Schulten, J. Phys. Chem. **102**, 7640 (1998).
- ¹⁵(a) H. Nakatsuji, M. Komari, and O. Kitao, Chem. Phys. Lett. **142**, 447 (1987); (b) H. Nakatsuji, O. Kitao, and T. Yonezawa, J. Chem. Phys. **83**, 723 (1985); (c) H. Nakatsuji, J.-Y. Hasegawa, and M. Hada, *ibid*. **104**, 2321 (1996).
- ¹⁶ (a) J. F. Stanton and R. J. Bartlett, J. Chem. Phys. **98**, 7029 (1993); (b) S. R. Gwaltney, M. Nooijen, and R. J. Barlett, Chem. Phys. Lett. **248**, 189 (1996); (c) for a review of couple-cluster methods, see R. J. Barlett and J. F. Stanton in *Reviews of Computational Chemistry*, edited by K. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. 5.
- ¹⁷P. Jørgensen and J. Simons, Second Quantization-Based Methods in Quantum Chemistry (Academic, New York, 1981).
- ¹⁸A. E. Hansen and T. D. Bouman, Mol. Phys. **37**, 1713 (1979).
- ¹⁹J. D. Baker and M. C. Zerner, J. Phys. Chem. **95**, 8614 (1991).
- ²⁰ For the term i=j and a=b, using spin states or determinants yield the same result. This is because it is not possible to distinguish whether ϕ_i that was excited from $\psi_{ia}^A \psi_0^B$ was of α or β spin in forming $\psi_{iaia}^A \psi_{kc}^B$. For the case i=j, $a\neq b$, or $i\neq j$, a=b, it does matter. Using spin states yields 1/2 the result in Eq. (22).
- ²¹ (a) W. Kuhn, Z. Phys. **33**, 408 (1925); (b) H. A. Bethe, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Springer, Berlin, 1933), Part 1, Vol. 24.