

# Comment on “Intrinsic convergence in close-shell SCF calculations. A general criterion”

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observed solvent effect on oscillator strength. Previous investigators have demonstrated that first order perturbation theory is adequate for predicting solvent effects on transition energies.<sup>6</sup>

(iii) Abe's most serious criticism involves his perception that we neglected the effect of the solvent cavity field in our derivation. Abe's remark misses the point that our derivation<sup>1</sup> used first order perturbation theory to determine the local field experienced by the solute due to nearby solvent molecules. As we noted in our paper, our semiclassical derivation yields a result very similar in form to the equation derived by DeVoe and Tinoco to account for polynucleotide hypochromism in DNA.<sup>7</sup> DeVoe<sup>8</sup> has demonstrated that a classical local field treatment of hypochromism is physically equivalent to the corresponding first order perturbation treatment<sup>7</sup> and leads to the same expression. In other words, our semiclassical treatment can be viewed as a quantum mechanical "analog" to a classical local field treatment. While the classical approach may be easier to understand intuitively,<sup>8</sup> it can in no respect be inherently superior. We have not neglected local field effects, as claimed by Abe, but chose to evaluate the effect of the solvent induced field using a semiclassical first order perturbation treatment. Within the approximations outlined in Ref. 1, our final result [Eq. (24) of Ref. 1] is correct.

In conclusion, Abe's criticisms of the theoretical

treatment presented in Ref. 1 are unfounded. The introduction of  $n^2$  in the denominator of both the experimental and theoretical expressions for the oscillator strength cannot be justified. Apparently, it was the introduction of this factor which enabled Abe<sup>9</sup> to derive equations predicting a decrease in oscillator strength with increasing solvent refractive index even though he started with a theory which predicts an increase in local field strength under these conditions. Furthermore, his claim that we neglected local field effects is simply wrong. The calculation of the solvent induced field was the primary goal of the theoretical derivation presented in Ref. 1.

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## Comment on "Intrinsic convergence in close-shell SCF calculations. A general criterion"

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In the paper which is the subject of this comment,<sup>1</sup> Stanton discusses a criterion for establishing the intrinsic convergence character of a closed-shell SCF calculation. This is discussed in terms of the absolute value of the largest eigenvalue of a matrix  $Q$ , which in Stanton's notation is written as

$$Q_{i,j,rs} = -(\epsilon_i - \epsilon_j)^{-1} (4[ij||rs] - [ir||js] - [is||jr]), \quad (1)$$

where  $i$  and  $r$  stands for virtual, and  $j$  and  $s$  for occupied molecular orbitals, respectively.

However, in that paper no relation is sought between intrinsic nonconvergence in this type of calculations and possible instabilities of the Hartree-Fock SCF wave functions in molecular systems. Cizek and Paldus<sup>2</sup> have, some time ago, studied and classified these instabilities. In particular, in close-shell SCF calculations they are classified as singlet instabilities and conditions stated in Ref. 2 have extensively been used in problems related to lattice instabilities of conjugated hydrocarbons.<sup>2-10</sup> These singlet stability conditions can be expressed through the positiveness of all eigen-

values of a certain matrix  $E$ ,<sup>2,10</sup> which, with the notation of Ref. 1, can be written as

$$E_{i,j,rs} = (\epsilon_i - \epsilon_j) \delta_{ij} \delta_{rs} + (4[ij||rs] - [ir||js] - [is||jr]). \quad (2)$$

It is straightforward to show that when the convergence criterion of Eq. (1) is satisfied, then the singlet stability condition, Eq. (2), is obtained, i.e., if the classical algorithm converges then one can be sure that the corresponding closed-shell energy is a minimum in the allowed space of singlet functions. This can be accomplished closely paralleling the discussion of the equivalence between nonsinglet instabilities and the convergence criterion of a CHF calculation of the Fermi contact term of spin-spin coupling constants, given in a previous paper of this Laboratory.<sup>11</sup> However, it must be stressed that these considerations are limited only to solutions that satisfy the *aufbau* principle.

Finally, it would be interesting to point out that caution should be taken when forcing the convergence<sup>1,12</sup>

in closed-shell SCF calculations. This is especially important when a solution with a broken symmetry is found, a case early discussed by Löwdin<sup>13,14</sup> as showing the presence of an instability of the singlet-type. In such cases the Hartree-Fock wave function is considered to be a poor approximation to the actual one.

Following Stanton,<sup>1</sup> the first order error in the wave function at iteration number  $i$ , may be written as

$$M^{(i)} = QM^{(i-1)}, \quad (3)$$

where  $M^{(i-1)}$  is the matrix error corresponding to the former cycle. This matrix  $Q$  can be written as the product between a symmetric matrix  $S$  and a diagonal positive matrix  $D$ ; provided the *aufbau* principle is followed:

$$D_{ij, mn} = (\epsilon_i - \epsilon_j)^{-1} \delta_{jk} \delta_{im}, \quad (4)$$

$$S_{m, n, r, s} = - (4 [mk || rs] - [mr || ks] - [ms || kr]), \quad (5)$$

where  $i$ ,  $m$ , and  $r$  represent virtual molecular orbitals, and  $j$ ,  $k$ , and  $s$ , represent occupied molecular orbitals.

Matrices  $Q$  and  $E$  of Eqs. (1) and (2), respectively, can be written in terms of  $D$  and  $S$ :

$$Q = DS, \quad (6)$$

$$E = D^{-1} - S. \quad (7)$$

Premultiplying by  $D^{-1/2}$  and inserting the unity matrix  $D^{1/2}D^{-1/2}$  Eq. (3) is expressed as

$$D^{-1/2}M^{(i)} = (D^{1/2}SD^{1/2})D^{-1/2}M^{(i-1)}. \quad (8)$$

Conditions on  $Q$  for obtaining convergence in a closed-shell SCF calculation as described in Ref. 1, are also valid for the matrix  $D^{1/2}SD^{1/2}$ . Therefore, convergence will be obtained when its largest absolute eigenvalue is smaller than unity.

Using Eq. (7), the matrix  $E$  can be written as

$$E = D^{-1} - S = D^{-1/2}(1 - D^{1/2}SD^{1/2})D^{-1/2}, \quad (9)$$

if all  $D^{1/2}SD^{1/2}$  eigenvalues are smaller than unity,

in absolute value, those corresponding to the matrix  $1 - D^{1/2}SD^{1/2}$  will be positive, and so will be those of matrix  $E$ , since a pre- and a post-multiplication by  $D^{-1/2}$  does not modify the sign of its eigenvalues. As this result becomes the condition for a singlet stable closed-shell SCF wave function,<sup>10</sup> it is concluded that if the classical algorithm converges, then one can be sure that the corresponding closed-shell energy is a minimum in the allowed space of singlet functions. However, the converse does not hold because the positiveness of all eigenvalues of  $E$  does not imply that all eigenvalues of  $D^{1/2}SD^{1/2}$  have absolute values smaller than unity, since there is no *a priori* reason of being matrix  $D^{1/2}SD^{1/2}$  positive definite. In fact, eigenvalues of this matrix can be negative as shown in Ref. 12, and in this case energy stability conditions can be satisfied, although algorithmic instabilities may be present. According to results of Refs. 12 and 15, it is very likely that such cases are related to the existence of energy stable solutions that do not satisfy the *aufbau* principle.

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## Parametrization of the CsNpF<sub>6</sub> optical spectrum

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The optical spectra of actinide ions are often difficult to interpret. This is partly due to the difficulty of obtaining a proper identification of the spectral lines and partly because the fitting space may have more than one minimum of the sum of squared deviations. For these reasons it is always suspicious when the experimental data for a particular system are fitted to parameters which are very different to those which have been shown to be appropriate for a range of similar systems. We have re-examined the recent work of Hecht *et al.*<sup>1</sup> on

Np<sup>5+</sup> in CsNpF<sub>6</sub> in this light with the aim of discovering the reason why their spectroscopic parameters should be so different from those obtained for other actinide ions (see Table I, noting particularly the values of  $\alpha$ ,  $\beta$ , and  $\gamma$  in column 1).

As a first step a matrix diagonalization program was written for  $f^2$  systems in cubic crystal fields in order to check the calculational aspects of the work of Hecht *et al.*<sup>1</sup> Using their fitted parameters we have verified