

Original Investigations

Transition Functional Schemes for Molecular Transition Energies

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Two different transition functionals are used to calculate the first and second ionization potentials of water. The results compare favourably with more costly ΔE_{SCF} results. Methods of dealing with convergence problems are discussed.

1. Introduction

Interest in direct calculation of transition energies has been increased greatly by advances in various kinds of electron spectroscopies. At their most sophisticated level, direct methods for calculation of ionization potentials, excitation energies, transition energies arising out of Auger, shake-up, or shake-off processes, etc., involve field theoretic and many-body methods [1]. In principle, these methods allow calculation of the desired transition energies to arbitrary accuracy, subject only to the practical limitations imposed by available computing resources.

A simpler direct method for calculation of transition energies, which involves only SCF theory, was proposed by Goscinski et al. [2]. This “transition operator” method was then generalized by Pickup et al. [3, 4]. The aim of this method is to mimic the result of separate SCF calculations for each of the initial and final states by a single SCF calculation using a suitably interpolated energy functional. The transition operator method has now been used in calculations on atomic and molecular systems for a fairly wide class of transitions [4, 5].

One of the results of the generalization achieved in [3] was a realization that the interpolation of the energy functionals of two states of a system to obtain a

transition functional may be carried out in more than one way [6]. In this paper, we present the results of applying two different transition functional schemes to the calculation of a selection of molecular ionization potentials. The accuracy of these methods is demonstrated by comparison with the corresponding ΔE_{SCF} results. Finally, we will make some comments about computational difficulties encountered in carrying out calculations for more complicated transition processes.

2. Basic Theory

We are interested in approximate representations of two states A and B, the energy functionals of which can be expressed in the form¹,

$$\tilde{E}_u = \sum_P \nu_P^u \text{tr} \tilde{\mathbf{R}}_P^u \mathbf{h}_P^{ad(u)}(\tilde{\mathbf{R}}^u), \quad u = \text{A or B} \quad (1)$$

where the ‘‘shell’’ density matrices²

$$\tilde{\mathbf{R}}_P^u = \sum_{p \in P} \tilde{\mathbf{T}}_P^u \tilde{\mathbf{T}}_P^{u\dagger} \quad (2)$$

are expressed in terms of the columns $\tilde{\mathbf{T}}_P^{(u)}$ of the molecular orbital expansion coefficients in the Roothaan LCAO formalism [8].

Not every trial wavefunction gives rise to this kind of simple ‘‘density type’’ energy functional. Nevertheless, all pure spin wavefunctions derived from a single orbital configuration, regardless of the number of open shells, have this property [21]. The only exceptions arise when spatial symmetry is imposed on a configuration with an incompletely filled degenerate shell arising from a non-Abelian point group.

The additive shell energy matrices in Eq. (1) are

$$\mathbf{h}_P^{ad(u)}(\tilde{\mathbf{R}}^u) = \mathbf{h} + \frac{1}{2} \tilde{\mathbf{G}}_P^u \quad (3)$$

Here \mathbf{h} is the bare nucleus or core matrix. The two-electron interactions are represented by the expressions

$$\tilde{\mathbf{G}}_P^u = \sum_Q [a_{PQ}^u \mathbf{J}(\tilde{\mathbf{R}}_Q^u) + b_{PQ}^u \mathbf{K}(\tilde{\mathbf{R}}_Q^u)] \quad (4)$$

where \mathbf{J} and \mathbf{K} are the usual Coulomb and exchange matrices [7]. The fractional occupation numbers, ν_P^u , are a direct reflection of the orbital occupations for the state. The parameters a_{PQ}^u and b_{PQ}^u are determined by both the occupation scheme and the spin coupling in the corresponding states.

Energy functionals of the form (1) can be made stationary with respect to orbital (or density matrix) variations using either the so-called coupling operator

¹ We distinguish trial functionals and densities with a tilde. The stationary quantities have the tilde removed.

² The energy functionals (1) are invariant against unitary transformations which mix orbitals in a single shell. These unitary symmetries can be said to define the shell structure.

formalism originally due to Roothaan [8], or using the effective Hamiltonian method of McWeeny [9, 10]. ΔE_{SCF} transition energies are then calculated by subtraction of the separately optimized state energies.

In the conventional transition functional approach [2, 4], however, one attempts to obtain the same information out of a single optimization of a linear energy interpolation functional of the form

$$\tilde{E}_{(\lambda)}^{\text{lin}} = \left(\frac{1}{2} + \lambda\right)\tilde{E}_a + \left(\frac{1}{2} - \lambda\right)\tilde{E}_b. \quad (5)$$

Using perturbation theory, it can be shown that the orbitals which make the particular choice $\tilde{E}_T^{\text{lin}} = \tilde{E}_{(0)}^{\text{lin}}$ stationary have special properties, and numerical experience shows they give very accurate estimates of the transition energy when compared with the ΔE_{SCF} method [3, 4]. The high accuracy obtained in practice using the linear energy interpolation formalism has been amply demonstrated for a variety of open shell systems [5].

It is natural to enquire whether the conventional interpolation scheme is uniquely useful. An obvious alternative to (5) is to interpolate only the numerical parameters ν_P^u , a_{PQ}^u , and b_{PQ}^u , in the specification of the energy (1) of the two states. Thus, we can write

$$\left. \begin{aligned} \nu_P(\lambda) &= \left(\frac{1}{2} + \lambda\right)\nu_P^a + \left(\frac{1}{2} - \lambda\right)\nu_P^b \\ a_{PQ}(\lambda) &= \left(\frac{1}{2} + \lambda\right)a_{PQ}^a + \left(\frac{1}{2} - \lambda\right)a_{PQ}^b \\ b_{PQ}(\lambda) &= \left(\frac{1}{2} + \lambda\right)b_{PQ}^a + \left(\frac{1}{2} - \lambda\right)b_{PQ}^b \end{aligned} \right\}. \quad (6)$$

When inserted into a general energy expression of the form of Eq. (1), these interpolated parameters define what will be called a non-linear energy interpolation functional. The resulting transition energy expression is quadratic in λ , rather than linear as in Eq. (5). That is, we have

$$\tilde{E}_{(\lambda)}^{\text{non-lin}} = \tilde{E}_T^{\text{non-lin}} + \lambda \widetilde{\Delta E} + \lambda^2 \widetilde{\Delta^2 E} \quad (7)$$

where the transition functional, $\tilde{E}_T^{\text{non-lin}} = \tilde{E}^{\text{non-lin}}(0)$, is not in general identical to \tilde{E}_T^{lin} . The quantities appearing in (7) can be written as³

$$\begin{aligned} \widetilde{\Delta E} &= \tilde{E}_a - \tilde{E}_b \\ \widetilde{\Delta^2 E} &= 2(\tilde{E}_a + \tilde{E}_b) - 4\tilde{E}_T. \end{aligned} \quad (8)$$

Now, the stationary value of (7) depends upon λ in two ways, firstly *explicitly* through the linear and quadratic dependence shown, and secondly *implicitly*

³ These relations can be deduced by noticing that, in general

$$\tilde{E}_a = \tilde{E}\left(\frac{1}{2}\right)$$

$$\tilde{E}_b = \tilde{E}\left(-\frac{1}{2}\right)$$

and

$$[\tilde{E}(\lambda) - \tilde{E}(-\lambda)] = 2\lambda \Delta \tilde{E}$$

$$[\tilde{E}(\lambda) + \tilde{E}(-\lambda)] - 2\tilde{E}(0) = 2\lambda^2 \Delta^2 \tilde{E}$$

because the stationary densities $\{\mathbf{R}_p(\lambda)\}$ change with the energy functional as λ is varied. The stationarity of the energy functional ensures that variations in $E_{(\lambda)}^{\text{non-lin}}$ from this latter source vanish. This statement is just the Hellman–Feynman theorem in Eq. (11) of [3] (q.v. for details), i.e. the total differential

$$\frac{dE_{(\lambda)}^{\text{non-lin}}}{d\lambda} = \frac{\partial E_{(\lambda)}^{\text{non-lin}}}{\partial \lambda} = \Delta E + 2\lambda^2 \Delta^2 E \quad (9)$$

where the symbol $\partial/\partial\lambda$ implies explicit differentiation, only, of Eq. (7) with respect to λ . The exact ΔE_{SCF} energy difference is then

$$E_a - E_b = \int_{-1/2}^{+1/2} \frac{dE_{(\lambda)}^{\text{non-lin}}}{d\lambda} d\lambda = \int_{-1/2}^{+1/2} [\Delta E(\{\mathbf{R}_P(\lambda)\}) + 2\lambda^2 \Delta^2 E(\{\mathbf{R}_P(\lambda)\})] d\lambda \quad (10)$$

$$\sim \Delta E(\{\mathbf{R}_P(0)\}) = E_a(\{\mathbf{R}_P^T\}) - E_b(\{\mathbf{R}_P^T\}) \quad (11)$$

where the approximation inherent in (11) has the same status, in terms of perturbation theory, as the transition approximation E_T^{lin} for the linear case. The non-linear estimate of ΔE_{SCF} energy difference is then obtained by finding the orbitals which make the functional $E_T^{\text{non-lin}}$ stationary, and with those orbitals, calculating ΔE as given in Eq. (11) above. This procedure is no more complicated than the original linear method.

3. Application to a Configurational Averaged Energy Functional

Configurationally averaged many-shell SCF procedures [9] are often both convenient and sufficiently accurate for calculating energies of open shell systems [11, 18]. In such a case, the parameters appearing in Eq. (1) are given simply by,

$$\nu_P = n_P/m_P, \quad (12)$$

$$a_{PP} = \nu_P' = 2(n_P - 1)/(2m_P - 1),$$

$$a_{PQ} = \nu_P(P \neq Q), \quad b_{PQ} = -\frac{1}{2}a_{PQ}(\forall P, Q). \quad (13)$$

Here, n_P is the number of electrons in shell P , and m_P is the number of orbitals defining that shell. Using Eq. (13), it is easily shown that the interpolation scheme (6) is completely equivalent here to

$$n_P(\lambda) = (\frac{1}{2} + \lambda)n_P^a + (\frac{1}{2} - \lambda)n_P^b \quad (14)$$

which is a direct interpolation of electronic occupation numbers specifying the states involved in the transition.

The energy functional to be optimized can now be written as

$$\tilde{E}_T^{\text{non-lin}} = \text{tr} \sum_P \nu_P^T \tilde{\mathbf{h}}_P^{ad(T)} \quad (15)$$

where

$$\tilde{\mathbf{h}}_P^{ad(T)} = \mathbf{h} + \frac{1}{2}\tilde{\mathbf{G}}_P^T \quad (16)$$

with

$$\tilde{\mathbf{G}}_P^T = \nu_P^{T'} \mathbf{G}(\tilde{\mathbf{R}}_P) + \sum_{Q(\pm P)} \nu_Q^T \mathbf{G}(\tilde{\mathbf{R}}_Q) \quad (17)$$

$$G(\mathbf{R}) = J(\mathbf{R}) - \frac{1}{2}K(\mathbf{R})$$

and

$$\nu_P^T = \frac{1}{2}(\nu_P^a + \nu_P^b), \quad \nu_P^{T'} = \frac{1}{2}(\nu_P^{a'} + \nu_P^{b'}) \quad (18)$$

The first order variation of $\tilde{E}_T^{\text{non-lin}}$ produced by a variation in the transition density matrices $\{\tilde{\mathbf{R}}_P^T\}$, is then,

$$\delta \tilde{E}_T^{\text{non-lin}} = \text{tr} \sum_P \nu_P^T \delta \tilde{\mathbf{R}}_P \tilde{\mathbf{h}}_P^T \quad (19)$$

where $\tilde{\mathbf{h}}_P^T$ is the transition Fock operator corresponding to shell P , and is given by,

$$\tilde{\mathbf{h}}_P^T = \mathbf{h} + \tilde{\mathbf{G}}_P^T \quad (20)$$

According to the effective Hamiltonian formalism of McWeeny [7], the orbitals which make $\tilde{E}_T^{\text{non-lin}}$ stationary (as well as satisfying the usual orthonormality constraints) are self-consistent eigenvectors of the matrix,

$$\bar{\mathbf{h}}_T^{\text{non-lin}} = \sum_P \tilde{\mathbf{R}}_P \mathbf{d}_P \tilde{\mathbf{R}}_P + \sum_{P,Q} b_{PQ} \tilde{\mathbf{R}}_P (\nu_P^T \tilde{\mathbf{h}}_P^T - \nu_Q^T \tilde{\mathbf{h}}_Q^T) \tilde{\mathbf{R}}_Q \quad (21)$$

The sums in P and Q here are over all shells. The requirement that $\delta \tilde{E}_T^{\text{non-lin}}$ vanish in first order subject to constraints is equivalent to the requirement that all of the matrix triple products in the second summation of (21) vanish. The numerical parameters b_{PQ} (damp factors) and the ‘‘diagonal part’’ matrices, \mathbf{d}_P , are not restricted in any way by the variational requirements. In practice, they generally have a marked effect on rates of convergence and the nature of the stationary solution to which the iterative calculation eventually converges [12]. At self-consistency, the effective operator (21) becomes

$$\bar{\mathbf{h}}_T^{\text{non-lin}} = \sum_P \mathbf{R}_P^T \mathbf{d}_P \mathbf{R}_P \quad (22)$$

Here, the tildes have been dropped from the density matrices, because they now correspond to a stationary value of the energy functional.

Finally, we note one further simplification in the expression for the transition energy when a configurationally averaged energy functional is used. Using Eq. (12) and Eq. (13), the transition energy can be re-written as

$$E_a(\{\mathbf{R}_P^T\}) - E_b(\{\mathbf{R}_P^T\}) = \text{tr} \sum_P \left(\mathbf{h}_P^T + \frac{1}{2m_P - 1} \mathbf{G}(\mathbf{R}_P^T) \right) \mathbf{R}_P^T (\nu_P^a - \nu_P^b) \quad (23)$$

where the P 'th shell Fock matrix is given in Eq. (20) above. Thus, with the choice,

$$\mathbf{d}_P = \mathbf{h}_P^T + \frac{1}{2m_P - 1} \mathbf{G}(\mathbf{R}_P) \quad (24)$$

in (21), then at self-consistency,

$$\begin{aligned}
 E_a(\{\mathbf{R}_P^T\}) - E_b(\{\mathbf{R}_P^T\}) &= \text{tr} \sum_P \mathbf{d}_P \mathbf{R}_P^T (\nu_P^a - \nu_P^b) \\
 &= \sum_P (\nu_P^a - \nu_P^b) \sum_{p \in P} \varepsilon_P
 \end{aligned}
 \tag{25}$$

where the ε_p are the orbital energies (the eigenvalues of $h_T^{\text{non-lin}}$ at self-consistency) corresponding to the p th eigenfunction of (21) in shell P , given Eq. (24). Thus, for this configurationally averaged energy functional, the transition energy may be calculated as a weighted sum of orbital energies, rather than by using the somewhat more complicated Eq. (11). Formulas like Eq. (25) can be written down for transitions between states with exact spin symmetry if their energy functionals satisfy the definitions in Eqs. (12) and (13). Examples of these are closed shell singlets, and doublet states arising out of configurations with one unpaired electron outside of a closed shell. Any pair of pure spin states which have SCF energy functionals of the form (1) can be treated using either the linear or non-linear methods, but the final energy difference will have to be calculated via Eq. (11) in general, rather than Eq. (25), since the reduction to (25) depends upon (12) and (13).

4. Computational Example

To illustrate the agreement between ΔE_{SCF} results and corresponding linear and non-linear interpolation results, a series of calculations were performed for the water molecule. A double zeta basis was used⁴. The calculations were carried out using the procedures recommended in [12] with regard to choice of damp-factor signs. Convergence was assessed using the stationary conditions themselves rather than arbitrary quantities, such as steplengths. The diagonal factors were chosen to satisfy Koopmans' theorem for the various shells [12]. The results for the removal of a single electron from the ground state molecule are listed in Table 1, and those for the removal of two electrons from the same orbital are given in Table 2. In all cases, the initial state in the transition was taken to be the molecular ground state. Absolute errors in the linear and non-linear interpolation results compared with the ΔE_{SCF} results are also listed. While these absolute errors tend to increase somewhat as the transition energy increases, the relative error actually decreases rather markedly with increasing transition energy. Also, the discrepancy between the linear and non-linear results and the ΔE_{SCF} results are seen to be not significant in relation to the discrepancy between the ΔE_{SCF} results and experimental results. For the single electron ionizations, the non-linear method mimics the ΔE_{SCF} method marginally better than does the linear method, while for the two electron ionizations, the opposite is true. In either case, there is very little to choose between the two transition functional methods.

⁴ The exponents for the 1s orbitals on the hydrogen atoms used were 1.33 and 2.47. Those for the oxygen atom were taken from Huzinaga, STO (4s, 2p) [13]. The geometry used for $R_{\text{OH}} = 1.8111$ a.u., $\theta_{\text{HOH}} = 104^\circ 27'$ (see Chong, [14]).

Table 1. (Energies in eV.)

Final state	ΔE_{SCF}	Linear calculations	Non-linear calculations	Exp. [16]
$1B_1^*$	11.443	11.521 (+0.078)	11.399 (-0.044)	12.6
$3A_1^*$	13.226	13.384 (+0.158)	13.179 (-0.047)	14.7
$1B_2^*$	17.997	18.073 (+0.076)	17.961 (-0.036)	18.4
$2A_1^*$	35.066	35.164 (+0.098)	34.992 (-0.074)	32.2
$1A_1^*$	539.964	540.343 (+0.379)	539.852 (-0.112)	539.7

Comparison of linear and non-linear transition functional calculations with ΔE_{SCF} calculations for water molecule ionization potentials. Energies are in eV, and absolute errors (from ΔE_{SCF}) are quoted in brackets.

Table 2. (Energies in eV.)

Final state	ΔE_{SCF}	Linear calculations	Non-linear calculations	Exp.*
$1B_1^{**}$	40.416	40.110 (-0.306)	39.967 (-0.449)	41.1
$3A_1^{**}$	44.087	43.815 (-0.272)	43.645 (-0.442)	45.9
$1B_2^{**}$	51.818	51.678 (-0.140)	51.432 (-0.386)	53.0
$2A_1^{**}$	88.372	88.228 (-0.144)	87.653 (-0.719)	88.9
$1A_1^{**}$	1172.474	1173.120 (+0.646)	1170.917 (-1.557)	—

Calculations for water double *IPs* in eV. Absolute errors over ΔE_{SCF} are given in parentheses.

* Values obtained from a poorly resolved auger spectrum [17] by subtracting the experimental value quoted for the $1A_1^*$ IP in Table 1. These values are quoted merely as a rough guide.

5. Practical Considerations and Discussion

The linear and non-linear interpolation methods can also clearly be applied to the calculation of Auger, shake-up, and shake-off transition energies. As in ΔE_{SCF} calculations, though, it may not be at all straightforward to achieve a convergent iterative calculation to a particular state (or transition state). Since at least one (and possibly both) of the states involved in these calculations will not be the ground state of the system, such calculations generally involve an attempt to converge onto a saddle point on the SCF energy surface, rather than to some local or global minimum. It is therefore of great importance to ensure that the orbital mixings implied by the diagonalization of Eq. (21) or its equivalent produce energy variations of the appropriate sign. The fact that the functional being optimized is no longer necessarily to be minimized with respect to all variations is not a catastrophe, but it does mean that SCF programs cannot be used quite so much as black boxes for these calculations as they can be for many simple closed shell ground states.

In the calculations reported above, the closed shell $2A_1^{**}$ state gave the greatest convergence difficulty. General considerations of the iterative procedure [15] indicate that any configuration in which an unoccupied orbital is intermediate in

energy between two occupied orbitals of the same symmetry, may well present serious convergence problems. Nevertheless, for the $2A_1^{**} \leftarrow G.S.$ process, the linear and non-linear interpolation calculations presented no particular difficulties. For other transitions, the SCF calculations converged more easily than one or the other (or even both) of the transition functional calculations.

The point is that while linear and non-linear interpolation calculations for a complicated electronic rearrangement in a system may not converge easily, these same convergence problems are also experienced in the corresponding ΔE_{SCF} calculations. If a transition functional approach is used, it is necessary to achieve only a single convergent iterative calculation, rather than two, as for ΔE_{SCF} calculations. As the results in Tables 1 and 2 amply demonstrate, this doubling of computational efficiency leaves the accuracy of the results virtually unaffected, for practical purposes.

Subsequent practical experience, however, indicates that convergence problems for many calculations on excited states may be significantly reduced by transforming the integrals to an orthogonal basis. This has the effect of eliminating large components from projections onto unoccupied spaces, which make many numerical algorithms for solving the stationary equations ill-conditioned. Improvement in convergence is so dramatic for a wide number of excited state calculations that many of the difficulties experienced in the above series could no doubt have been reduced markedly were they to be repeated in this manner. However, in calculations involving large numbers of basis functions, the cost of the transformation to an orthogonalized basis may be justified only if a large number of SCF calculations are contemplated.

It is well-known that ΔE_{SCF} methods fail to give accurate estimates of valence shell molecular ionization potentials [19], and fail to explain the inner-valence range even qualitatively. Nonetheless, ΔE_{SCF} is a commonly used procedure for all kinds of transition energy calculations. Transition operator calculations have even formed the starting point for propagator calculations of molecular IP's, with impressive results [20].

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