Original Investigations

Approximate Energy Expression in the Calculation of Photoelectron Transition Energies

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The possibilities of using approximate self-consistent field energy functionals to reduce computation required in calculating photoelectron transition energies is examined. Numerical results for the H_2O molecule indicate that this is possible without unacceptable deterioration in accuracy of results in favourable cases.

Key Words: Photoelectron transition energies – Configurational average – Transition operator.

1. Introduction

In quantum chemistry, the calculation of energies of atomic or molecular systems invariably involves the evaluation, either directly or indirectly, of the energy expectation value (Ritz ratio),

$$E(\Psi) = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{1}$$

Here $\mathcal{H}$ is the hamiltonian operator for the system. It is well known that when the wavefunction Ψ is an eigenfunction of $\mathcal{H}$, small variations in Ψ affect the value of $E(\Psi)$ only in second order, that is,

$$E(\Psi + \delta \Psi) = E(\Psi) + \mathcal{O}(\delta \Psi^2). \tag{2}$$

This implies that the calculated energy may be quite insensitive to small inaccuracies in Ψ, as long as it is a reasonable approximation to the exact wavefunction.

In this note, we describe some useful consequences of this stability of $E(\Psi)$ which can be exploited in the calculation of molecular excitation energies using self-consistent field (SCF) methods. In these methods, Ψ is written as a single configuration function (that is, as a single determinant or as a linear combination of a small number of determinants with the linear expansion coefficients fixed by the spatial symmetry of the system). These determinantal functions are constructed out of one-electron functions (spin–orbitals) which are chosen to make $E(\Psi)$, Eq. (1), stationary with respect to any parameters appearing in the specification of the orbitals. The most commonly adopted parametrization is the LCAO (linear combination of atomic orbitals), which involves the expansion of the spatial parts, $\phi_p(r)$, of the orbitals in terms of a set of atomic orbitals, $\chi_q(r)$, defined on fixed centers,

$$\phi_p(r) = \sum_{q=1}^{m} \chi_q(r) T_{qp}. \tag{3}$$

The optimization of the energy $E(\Psi)$ with respect to the parameters $\{T_{qp}\}$ is typically carried out by converting the resulting stationary conditions into a pseudo-eigenvalue equation, which is solved iteratively [1]. This iterative determination of the SCF wavefunction itself accounts for most of the cost of these calculations, once the initial basis function integral generation has been done.

One way of reducing the computation involved in determining a series of energy levels for a particular system is to calculate sets of spin-orbitals which are good approximations to the optimum orbitals for more than one state. This would involve optimizing an energy functional constructed as a combination of energy functionals for two or more states. However it must be remembered that, in SCF theory, these orbitals are used in part to describe a time-averaged electronic field, and thus, this procedure can only be expected to work if the various states involved do not correspond to very different self-consistent fields. Once these optimal "average" spin-orbitals are obtained, they can be used to calculate the energies of each of the states involved using the true energy functions.

The most general SCF energy functional depending only on one-particle densities can be written [2],

$$E = \sum_{P} \nu_P \, tr \, \mathbf{R}_P \mathbf{h}_P^{ad}(\mathbf{R}) \tag{4a}$$

with

$$\mathbf{h}_P^{ad}(R) = \mathbf{h} + \tfrac{1}{2} \sum_{Q} [a_{PQ} \mathbf{J}(\mathbf{R}_Q) + b_{PQ} \mathbf{K}(\mathbf{R}_Q)]. \tag{4b}$$

In these expressions, the quantities $\{\nu_P\}$, $\{a_{PQ}\}$, and $\{b_{PQ}\}$, are numerical constants which are determined by the electronic occupations and spin coupling schemes.

The single particle density matrices, $\{\mathbf{R}_P\}$, are given in terms of the LCAO coefficients, Eq. (3), by

$$\mathbf{R}_P = \sum_{p \in P} \mathbf{T}_p \mathbf{T}_p^{\dagger}.$$

The matrix $\mathbf{h}$ is the nuclear framework hamiltonian, and $\mathbf{J}(\mathbf{R})$ and $\mathbf{K}(\mathbf{R})$ are the usual coulomb and exchange interaction matrices (see [1], page 114). The summations in Eqs. (4a, b) run over all non-empty shells of the system. We now consider two types of averages based on functionals of the form (4a, b).

2. Full Configurational Average

The energy functional to be optimized in this case consists of a weighted average of the functionals corresponding to all the distinct spin couplings for a given shell occupation scheme ([3], [4]). Denoting the number of electrons in shell P by n_p, and the number of spin orbitals in shell P by m_p, the constants in Eqs. (4a, b) are given simply as,

$$
\begin{aligned}
& \nu_P = n_P/m_P, \\
& a_{PP} = \nu'_P = 2(n_P - 1)/(2m_P - 1), \\
& a_{PQ} = \nu_Q, \quad (Q \neq P), \\
& b_{PQ} = -\tfrac{1}{2}a_{PQ}, \quad (\text{all } P, Q).
\end{aligned}
\tag{6}
$$

To illustrate the correspondence between exact pure-spin SCF results and results obtained using this configurational averaging scheme, a series of calculations were carried out on a selection of doubly ionized states of the H_2O molecule, in which two electrons have been removed from different orbitals[1]. When both singly occupied orbitals, ϕ_a and ϕ_b, are considered to be in the same shell, a total of four distinct pure-spin states are involved in this configurational averaging scheme. There is an open shell spin singlet, an open shell spin triplet, and two closed shell spin singlets corresponding to one of ϕ_a or ϕ_b being doubly occupied and the other empty. Denoting the exact spin-adapted energies of these four states by $^1E^{OS}$, $^3E^{OS}$, E_a^{CS}, E_b^{CS}, respectively, the functional, E^{CA}, to be optimized is

$$E^{CA} = \tfrac{1}{6}(^1E^{OS} + 3\,^3E^{OS} + E_a^{CS} + E_b^{CS}). \tag{7}$$

The results of the calculations are given in Table I for a series of states in which the canonical energies of the two orbitals from which electrons have been removed varies. The discrepancy between the spin-resolved configurational averaged results and the pure spin SCF results are seen to be generally very small indeed ($<0.01\%$) except when ϕ_a and ϕ_b are of drastically differing energies. The largest discrepancies occur for the $1B_1^* 1A_1^*$ state. This is due to the fact that the true self-consistent field after removal of two electrons from valence orbitals is very

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[1]   A double zeta basis set was used. 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) [5]. The geometry used was $R_{OH} = 1.8111$ a.u., $\theta_{HOH} = 104°27'$ (see [6]).

Table 1. Pure-spin SCF vs. spin-resolved configurationally averaged SCF. Total electronic energies (in a.u.) for a selection of double ion states of H_2O

State	Spin mult.	Pure spin	Resolved configurational averaged	Error
$1B_1^*3A_1^*$	3	-83.7833	-83.7808	0.0025
$1B_1^*3A_1^*$	1	-83.6790	-83.6780	0.0010
$1B_1^{**}$	1	-83.7002	-83.6992	0.0010
$3A_1^{**}$	1	-83.5653	-83.5603	0.0050
$1B_1^*1B_2^*$	3	-83.6135	-83.6132	0.0003
$1B_1^*1B_2^*$	1	-83.5427	-83.5412	0.0015
$1B_1^{**}$	1	-83.7002	-83.6980	0.0022
$1B_2^{**}$	1	-83.2812	-83.2784	0.0028
$1B_1^*2A_1^*$	3	-83.0240	-83.0230	0.0010
$1B_1^*2A_1^*$	1	-82.7305	-82.7333	-0.0028
$1B_1^{**}$	1	-83.7002	-83.6964	0.0038
$2A_1^{**}$	1	-81.9379	-81.9379	0.0000
$1B_1^*1A_1^*$	3	-64.3089	-64.3041	0.0048
$1B_1^*1A_1^*$	1	-64.1962	-64.1700	0.0262
$1B_1^{**}$	1	-83.7002	-83.4893	0.2109
$1A_1^{**}$	1	-42.0982	-41.9053	0.1929
$3A_1^*1B_2^*$	3	-83.5673	-83.5652	0.0021
$3A_1^*1B_2^*$	1	-83.4772	-83.4746	0.0026
$3A_1^{**}$	1	-83.5653	-83.5583	-0.0030
$1B_2^{**}$	1	-83.2812	-83.2784	0.0028

different from the field appropriate to the case when two electrons are removed from core orbitals. Indeed, it is surprising that a single set of orbitals can describe two such different states as the $1B_1^{**}$ and $1A_1^{**}$ as well as they do. Note again that in the column labelled "Pure Spin SCF" in Table 1, every entry required a complete orbital optimization, whereas only a single orbital optimization (followed by the evaluation of each of the functionals in Eq. (7)) was required for each group of four entries in the column labelled "Resolved Configurational Average".

3. Transition Operator Methods

In transition operator methods ([7], [8], [2]), one seeks optimal estimates for transition energies by making stationary an energy functional which is a combination of two functionals of the form (4a, b). Writing

$$E_u = \sum_P v_P^u \, tr \, \mathbf{R}_P^u \mathbf{h}_P^{ad(u)}(\mathbf{R}^u), \tag{8}$$

where $u = A, B$, denotes the two functionals involved, a linear transition

functional can be written as [8],

$$E^{\text{lin}}(\lambda) = (\tfrac{1}{2} + \lambda)E_A + (\tfrac{1}{2} - \lambda)E_B, \qquad -\tfrac{1}{2} \le \lambda \le \tfrac{1}{2}. \tag{9}$$

The two functionals, E_A and E_B, may represent systems differing in spin-symmetry type, shell occupation schemes, and even total numbers of electrons. These two individual functionals may represent pure spin and spatial symmetry states or they may be averages of some sort themselves. For Eq. (9) to be useable, only the total number of shells must be defined to be the same for the two systems.

A more subtle type of transition functional can be formed by interpolating the numerical constants $\{\nu_P\}$, $\{a_{PQ}\}$, and $\{b_{PQ}\}$, occurring in the functionals E_A and E_B. If E_A and E_B are configurational averages of the type described above, this is equivalent to interpolating the electronic occupations of the individual shells (see [2]). The resulting functional to be optimized is then a non-linear function of λ. In both the linear and non-linear interpolation cases mentioned here, use of $\lambda = 0$ leads to the optimal transition energy functional. The utility of transition operator methods when E_A and E_B are pure-spin energy functionals has already been demonstrated in a number of studies ([2], [8]). Instead, we consider here the situation in which E_A is the exact ground state energy functional for H_2O, and E_B is a configurationally averaged energy functional of the type described above. In Table 2 are listed calculated energies of ionization relative to the ground state for the same doubly ionized states as in Table 1. Results are given for pure-spin ΔE_{SCF} calculations, ΔE_{SCF} calculations using resolved configurationally averaged energy levels (as described in the previous section above), and transition functional calculations using both the linear interpolation scheme, Eq. (9), and the non-linear interpolation scheme described immediately above.

It is clear from these results that the additional level of approximation due to the interpolation of configurationally averaged energy functionals has had a significant effect on the accuracy of the calculated transition energies relative to the exact ΔE_{SCF} results. Whereas the ΔE_{SCF} results using resolved configurationally averaged transition energies are generally in error by significantly less than 0.1% (and perhaps more importantly, by less than 0.1 eV), the transition functional results exhibit errors five to ten (and more) times this size. Comparison with numerical results described in [2] seems to indicate that it is the energy functional interpolation part that is responsible for most of the large errors here, rather than the combination of configurational averaging and energy functional interpolation. It is just not possible for the same set of orbitals to give a good description of the self-consistent field corresponding to the ground state and that corresponding to a doubly ionized state. When errors in calculated transition energies begin to exceed 0.1 eV their usefulness in identifying features of photoelectron spectra becomes suspect.

4. Conclusions

The numerical results we have presented here illustrate both the potential usefulness and the limitations of SCF calculations involving approximate energy

Table 2. Ionization energies for a selection of doubly ionized states of H_2O. energies are given in eV., absolute errors relative to the pure spin ΔE_{SCF} brackets following the transition energies

State	Spin mult.	Pure spin ΔE_{SCF}	Resolved configurational averaged ΔE_{SCF}		Linear interpolation transition operator		Nonlinear interpolation transition operator	
$1B_1^*3A_1^*$	3	38.153	38.222	(−0.069)	30.162	(−1.009)	37.851	(0.302)
$1B_1^*3A_1^*$	1	40.994	41.020	(−0.026)	41.668	(−0.674)	40.639	(0.355)
$1B_1^{**}$	1	40.416	40.442	(−0.026)	41.401	(−0.985)	40.044	(0.372)
$3A_1^{**}$	1	44.087	44.222	(−0.135)	44.174	(−0.087)	43.645	(0.442)
$1B_1^*1B_2^*$	3	42.775	42.783	(−0.008)	43.561	(−0.786)	42.455	(0.320)
$1B_1^*1B_2^*$	1	44.703	44.742	(−0.039)	45.191	(−0.488)	44.185	(0.518)
$1B_1^{**}$	1	40.416	40.476	(−0.060)	42.444	(−2.028)	41.013	(−0.597)
$1B_2^{**}$	1	51.818	51.894	(−0.076)	51.406	(0.412)	50.599	(1.219)
$1B_1^*2A_1^*$	3	58.816	58.844	(−0.028)	59.619	(−0.803)	58.674	(0.142)
$1B_1^*2A_1^*$	1	66.804	66.728	(−0.076)	67.001	(−0.197)	66.234	(0.570)
$1B_1^{**}$	1	40.416	40.519	(−0.103)	41.383	(−0.967)	40.617	(0.210)
$2A_1^{**}$	1	88.372	88.371	(0.001)	88.087	(0.285)	87.254	(1.118)
$1B_1^*1A_1^*$	3	568.085	568.216	(−0.131)	569.829	(−1.744)	566.887	(1.198)
$1B_1^*1A_1^*$	1	571.150	571.864	(−0.714)	571.841	(−0.691)	569.488	(1.662)
$1B_1^{**}$	1	40.416	46.154	(−5.738)	32.793	(7.623)	30.920	(9.496)
$1A_1^{**}$	1	1172.460	1177.723	(−5.263)	1200.219	(−27.76)	1193.460	(−21.00)
$3A_1^*1B_2^*$	3	44.033	44.089	(−0.056)	45.094	(−1.061)	43.708	(0.325)
$3A_1^*1B_2^*$	1	46.484	46.555	(−0.071)	47.360	(−0.876)	45.998	(0.486)
$3A_1^{**}$	1	44.087	44.276	(−0.189)	45.683	(−1.596)	44.490	(−0.403)
$1B_2^{**}$	1	51.818	51.893	(−0.075)	51.825	(−0.007)	50.754	(1.064)

functionals. In cases in which the approximate functional to be optimized does not correspond to a greatly different self-consistent field from that appropriate to the true energy functional, the optimal "approximate" spin-orbitals obtained can give very good energies or transition energies when inserted in the true energy functionals. When an attempt is made to obtain a single set of orbitals applicable to systems which are too dissimilar, however, the usefulness of the results can deteriorate. This is demonstrated clearly by the above transition operator calculations, in which the approximate functionals optimized corresponded to systems differing by two electrons in ten. Results presented in [2] for transitions between the ground state and singly ionized states are much better, and thus it is likely that the transition functional methods would give more usable results here for transition energies between singly and doubly ionized systems. Such transition energies are required in the interpretation of Auger and related types of spectra.

The subject of Auger spectra is particularly important because of the difficulties in assignment where there are many lines, and many possible interpretations. There are a number of works in the literature which use SCF and Cl calculations as an aid in assignment [9–11]. It is not the purpose of the present paper to discuss the Auger spectrum of water, but to make the following general comments.

Ågren et al [9], and Hillier et al [10] have showed the effectiveness of a relatively limited "internal" Cl on top of SCF excited state calculations. We believe that our present results suggest that the extra orbital optimization of the MCSCF results of [11] is unnecessary. Furthermore, it seems probable that adequate assignments of Auger spectra can be made in the following manner. Firstly one carries out a configurationally averaged SCF for a group of states (such as $1B_1^*3A_1^*$ singlet and triplet, $1B_1^{**}, 3A_1^{**}$). Then an internal Cl both "resolves the configuration terms", and accounts for strong interactions between terms from other configurations. The usual approach adopted for Cl is to do a 4-index transformation to the MO basis, and then set the matrix elements. If a different Cl is required for each spin resolved SCF excited state this becomes very expensive. The use of configurationally averaged MOs reduces the number of 4-index transformations by a factor of four. Furthermore, for such a small Cl, especially with high symmetry, the Cl matrix may actually be constructed by scanning the AO integral files, using a generalisation [12] of the methods used to construct the Fock matrix. For very large basis sets (assuming the number of internal orbitals is small) this procedure is much cheaper than the standard one, since construction of the Cl matrix is equivalent to four or five iterations of the SCF procedure.

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