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Generalization of Slater's transition state concept

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We present a generalization of the transition state technique introduced by Slater for the calculation of many-electron relaxation effects accompanying electronic excitations in molecules and molecular simulations of solids. By making use of ground state information (which is generally available but not used in the Slater formulation) and transition states which are computationally cheaper (due to being closer to the ground state), the generalization permits the evaluation of excitation energies to be improved in any of three ways: (1) comparable accuracy for less computation; (2) improved accuracy for comparable computation; and (3) full Δ -SCF accuracy can be approximated with arbitrary precision with additional computation. In particular, we show that excitation energies of somewhat greater accuracy are obtained from self-consistent calculations performed for transition states corresponding to 2/3 of the transition rather than 1/2 of the transition as in the original formulation by Slater.

INTRODUCTION

In the past five years much progress has been made with respect to our understanding of electronic transitions in molecular systems.^{1,2} This progress, to a substantial extent, is due to the development and application of the so-called density functional theory of electronic structure.^{3,4} This theory makes practicable the calculation of electronic transition energies in relatively large molecules and molecular simulations of solids. A particularly important advantage of the new theory is the relative ease and accuracy with which the relaxation of the electrons not directly involved in the transition can be calculated. The accurate calculation of relaxation effects utilizes the "transition state" concept due to Slater.^{3,5} The generalization of this concept is the subject of this paper. We show that by taking a slightly different point of view the accuracy of the Slater technique can be increased without additional computation. Of greater practical importance, however, because the existing transition state technique is already quite accurate, we show that the accuracy of the present technique can be obtained with substantially less computational effort.

The paper is organized as follows. In Sec. I, we review the transition state concept as introduced by Slater. In Sec. II, we generalize the concept and present a formula for electronic transition energies which requires the same computational effort as Slater's but which is more accurate. In Sec. III, we present the results of numerical calculations and a formula for transition energies which provides the same accuracy as the Slater technique with less computational effort.

I. SLATER'S TRANSITION STATE

The objective of Slater's transition state³ is the accurate evaluation of electronic excitation energies of finite molecular systems. An excitation energy $\hbar\omega$ is the difference in the total energy (Δ -SCF) of the electronic system before and after the excitation,

$$\hbar\omega = E_{\text{final}} - E_{\text{initial}} \quad (1.1)$$

If the system contains more than a few electrons, E_{final} and E_{initial} are both very much larger than most of the $\hbar\omega$'s of interest, so that the straightforward evaluation of $\hbar\omega$ using Eq. (1.1) in conjunction with numerically computed total energies involves a great deal of numerical cancellation, thereby requiring extremely accurate evaluation of E_{final} and E_{initial} . Slater has shown that most of this cancellation can be avoided if the total energies are calculated using the relatively new theory of electronic structure, the density functional formalism, of which Slater's X_α formalism is the most highly exploited particular variation. The essential property of this formalism that makes the transition state notion possible is the fact that the total energy of the system is an analytic function of each of a set of one-electron-like occupation numbers

$$E = E(n_1, n_2, \dots, n_N) \equiv E(\mathbf{n}) \quad (1.2)$$

The occupation numbers n_i indicate the contribution to the electron density $\rho(\mathbf{r})$ of each of a set of one-electron-like molecular orbitals $\{\psi_i(\mathbf{r})\}$,

$$\rho(\mathbf{r}) = \sum_i n_i |\psi_i(\mathbf{r})|^2 \quad (1.3)$$

The analyticity of the total energy in the occupation numbers permits the Taylor series expansion of E_{final} and E_{initial} about a common point in occupation number space, thereby effecting the numerical cancellation analytically. Consider for example the following ionizing transition

$$\hbar\omega = E(0, 1, 1, \dots, 1) - E(1, 1, 1, \dots, 1) \quad (1.4)$$

If we expand both the initial and final energies about the common point in \mathbf{n} space $\{n_i\} = (\frac{1}{2}, 1, 1, \dots, 1)$, then all the even order terms in the expansion of $\hbar\omega$ in powers of δn_i are zero leaving,

$$\hbar\omega = \partial E / \partial n_1 + \text{terms of order } (\delta n_1)^3 \quad (1.5)$$

It is a further convenience of the approximate density functional schemes now in use (e.g., the X_α method and the Kohn-Sham method) that the required partial derivatives of the total energy are given by the theory in the

form of one-electron-like molecular orbital energies

$$\partial E / \partial n_i = \epsilon_i, \quad (1.6)$$

so that excitation energies are obtained from the theory by performing self-consistent field calculations at intermediate values of the orbital occupation numbers. Slater's transition state consists of keeping only the first term in Eq. (1.5) thereby incurring an error of order δn^3 . In the next section, we show that the leading term in the error can be eliminated without additional computation.

II. GENERALIZED TRANSITION STATE

The simplest way of presenting our generalization of Slater's transition state concept is to consider the same specific example we considered in Sec. I, that of an ionization excitation. We begin by rewriting Eq. (1.1) as follows

$$\hbar\omega = \int_1^0 dn_1 \frac{\partial E(\mathbf{n})}{\partial n_1}, \quad (2.1)$$

which using Eq. (1.6) we can rewrite as follows,

$$\hbar\omega = \int_1^0 dn_1 \epsilon_1(\mathbf{n}). \quad (2.2)$$

The path through \mathbf{n} space traversed in the course of a particular transition can be considered as a reaction coordinate. Equation (2.2) for the excitation energy shows that we can interpret Slater's transition state as the "midpoint" numerical integration formula,

$$\int_a^b dx f(x) \approx (b-a)f((a+b)/2) \quad (2.3)$$

applied to the integral in Eq. (2.2).

Equation (2.2) not only allows us to reinterpret Slater's technique, but also shows us that the transition energy $\hbar\omega$ can be evaluated to any accuracy we like by performing the integral over the reaction coordinate with as much numerical sophistication as required. In particular, we now show that if one is willing to perform the self-consistent field calculation required to evaluate the integrand in Eq. (2.2) at a single intermediate point along the reaction coordinate, then the midpoint (Slater's method) is not the optimum strategy. The reason that the midpoint is not the best is that the integrand is always known at one end (the ground state) of the reaction coordinate. Thus, if we restrict ourselves to one evaluation of the integrand at an intermediate position along the reaction coordinate (i.e., the same amount of work required by Slater's method), then the optimum strategy consists of determining the values of β and λ in the following numerical integration formula,

$$\int_A^B dx f(x) \approx (B-A) \{ \beta f(A) + (1-\beta) f[A + \lambda(B-A)] \}, \quad (2.4)$$

which eliminate as many terms as possible in the expansion of the error in powers of $B-A$. This can be accomplished by expanding both sides of Eq. (2.4) in powers of $B-A$ and equating the coefficients of each power. The fact the sum of the integration weights β and $1-\beta$ is unity guarantees that the lowest power of

$B-A$ in the error is 2. Equating the general term in the expansion of both sides of Eq. (2.4) leads to the equation

$$(k+1)^{-1} = (1-\beta)\lambda^k; \quad k > 0. \quad (2.5)$$

Since we have only two degrees of freedom (β and λ) we can only satisfy this relation for $k=1$ and $k=2$. This requires that $\beta = \frac{1}{4}$ and $\lambda = \frac{2}{3}$ and implies that the lowest power of $B-A$ in the error is 3. The coefficient of $(B-A)^3$ is proportional to d^3f/dx^3 ; for the midpoint formula on which Slater's method is based the error is proportional to $(B-A)^2 d^2f/dx^2$. (Slater's method is seen to result from setting $k=1$ and $\beta=0$ in equation 2.5 and is therefore the best that one can do using only the information provided by a single transition state calculation.) So, as expected, using the information available in the ground state calculation eliminates one additional term in the error. The corresponding expression for the excitation energy (ionization potential in our example) is

$$\hbar\omega \approx \frac{1}{4} \epsilon_1(1, 1, 1, \dots, 1) + \frac{3}{4} \epsilon_1(\frac{1}{3}, 1, 1, \dots, 1). \quad (2.6)$$

The generalization to excitations involving two or more orbital states is immediate; rather than obtaining the excitation energy from the intermediate state half way between the initial and final states as Slater's method prescribes, Eq. (2.6) tells us that a slightly more accurate value of $\hbar\omega$ is given by the sum of $\frac{1}{4}$ times the transition energy indicated by the ground state calculation and $\frac{3}{4}$ times the transition energy given by the "transition state" located $\frac{2}{3}$ of the way along the reaction coordinate connecting the ground state to the excited state.

III. NUMERICAL APPLICATIONS

We have applied our analysis of the excitation energy given in Sec. I and II to two ionizing excitations of a MoS_6^{8-} cluster used to simulate the crystalline compound MoS_2 . The relevance of this particular system to the subject of this paper is (1) it was conveniently available because one of us (R. dG.) is studying its electronic structure, and (2) it contains two qualitatively different kinds of electronic states, d states spatially localized on the molybdenum sites and spatially delocalized states arising from the sulfur p states. Therefore, we were able to study excitations accompanied by significantly different degrees of relaxation.

Figure 1 shows the variation of $\epsilon_i = \partial E(\mathbf{n}) / \partial n_i$ along the ionization reaction coordinate ($1 \geq n_i \geq 0$) for two states of the MoS_6^{8-} cluster. The state labelled p is a spatially delocalized A' state arising from atomic sulfur p states and the state labelled d is a A'_1 state of primarily d character and spatially localized on the molybdenum site. Figure 1 clearly exhibits the two aspects of relaxation discussed by Baerends and Ross² in their recent study of ionization potentials of small molecules. The bulk of the relaxation is common to all states of the cluster and stems from the change in total charge on the cluster due to ionization. The difference in relaxation experienced by states of differing degrees of localization is the physical quantity which is crucial to the interpretation of photoemission data, for example, because it determines the level ordering and spacing.

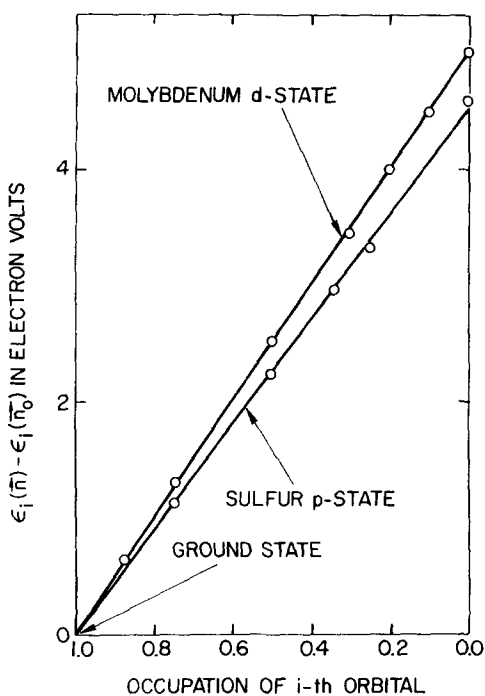


FIG. 1. Dependence of "one-electron" energies $\epsilon_i(\mathbf{n}) = \partial E_{\text{total}} / \partial n_i$ on the occupation of a localized d orbital and a delocalized p orbital in a Mo S_8^+ molecular cluster designed to simulate the solid compound MoS_2 . The many-electron relaxation energies are the areas under the respective curves. The circled points indicate areas independent self-consistent calculations; the lines were drawn through the points.

This difference appears in Fig. 1 as the difference in slope between the two curves. It is clearly seen that the difference in slope is a good deal smaller than the slope itself.

For the purposes of this paper the important point exhibited by Fig. 1 is the essential linearity of both curves. This linearity implies that the difference between Slater's prescription for the transition energy and our slightly more accurate prescription [Eq. (2.6)] is totally unimportant. The calculations required to construct Fig. 1 however suggest a much more practical exploitation of our generalized point of view. Self-consistent calculations for occupation numbers far away from the ground state are much more time consuming and costly because many more iterations are required to achieve self-consistency starting, as one must, from the ground state electron density or effective-one-electron potential. For systems exhibiting a linear dependence of $\epsilon_i(\mathbf{n}) = \partial E_{\text{total}} / \partial n_i$ on \mathbf{n} such as that seen in Fig. 1, the prescription for the excitation energy obtained by setting λ in Eq. (2.4) to a small value,

$$\tilde{\epsilon}_\omega \approx \epsilon(\mathbf{n}_0) + (2\lambda)^{-1} \{ \epsilon[\mathbf{n}_0 + \lambda(\mathbf{n} - \mathbf{n}_0)] - \epsilon(\mathbf{n}_0) \}, \quad (3.1)$$

will yield accurate excitation energies and greatly reduce the number of self-consistency interactions required to obtain them. In Eq. (3.1) \mathbf{n}_0 is the set of occupation numbers describing the ground state and \mathbf{n} the set describing the excited state. Note that Eq. (3.1) includes Slater's prescription ($\lambda = \frac{1}{2}$) as a special case. The leading term in the error incurred by the use of Eq. (3.1),

$$\text{error} \propto [\partial^3 E(\mathbf{n}) / \partial n^3] (\frac{1}{3} - \frac{1}{2}\lambda), \quad (3.2)$$

is seen to pass through zero for $\lambda = \frac{2}{3}$, which is the origin of Eq. (2.6), and to increase as λ is reduced toward zero. The loss of numerical significance involved in evaluating the difference $\epsilon[\mathbf{n}_0 + \lambda(\mathbf{n} - \mathbf{n}_0)] - \epsilon(\mathbf{n}_0)$ is the practical limit to the reduction of λ , not the gradual increase in the error seen in Eq. (3.2). In other words, the use of small λ is fundamentally extrapolation, a process which amplifies errors in the quantities upon which the extrapolation is based. Our limited numerical experience suggests that $\lambda \sim 0.1$ is a practical compromise.

Regarding the question of how generally can we expect the linearity exhibited in Fig. 1, we do not expect it to persist in small systems involving only a few electrons. Only additional calculations will reveal how small is small. If, as we suspect, nonlinearities in $\epsilon_i(\mathbf{n})$ as a function of \mathbf{n} decrease as the size of the molecule increases, then Eq. (3.1) will fortunately be of greatest utility where it is most needed, in calculations on large systems.

IV. CONCLUSIONS

We have presented a generalization of the transition state technique for the calculation of electronic excitations in molecular systems. We have shown that, compared to the original formulation by Slater, our generalized point of view can be exploited in three different ways. (1) The prescription for the excitation energy given in Eq. (2.6) eliminates the leading term in the error introduced in the Slater method with at most a marginal increase in computational effort. (The transition states required by Eq. (2.6) being farther from the ground state than those required by Slater's method may require more iterations to achieve self-consistency.) (2) Our own limited numerical experience suggests that the prescription for the excitation energies given in Eq. (3.1) is a substantial practical improvement over the Slater method in that it describes the same physical effect with essentially the same accuracy but with appreciably less computation. (3) As a matter of principle, we have shown that the transition state technique per se need not be approximate; the difference between final and initial total energies can be evaluated to any accuracy one desires merely by performing the integration in Eq. (2.1) with the required numerical precision. As a final comment, the linear dependence of $\epsilon_i(\mathbf{n}) = \partial E / \partial n_i$ on \mathbf{n} which our numerical examples display raises the hope that the relaxation energy can be evaluated by perturbation theory, a procedure which would eliminate the need for numerical transition state calculations altogether.

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