BRIEF REPORTS

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Slater transition-state band-structure calculations

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Slater's transition-state method enables one to calculate excitation energies by means of an artificial state that is halfway between the ground state of an atom or molecule and an excited state. This idea has been adapted to insulators and semiconductors with a band-structure model where a localized hole is created in one cell by removing charge from the top of the valence band and putting it in a delocalized state at the bottom of the conduction band. Significant improvements in calculated band gaps are obtained in most cases over conventional local-density calculations.

A persistent problem in the local-density theory[1] of electronic structure is that the eigenvalues of the one-electron Schrödinger equations do not give a good representation of electron binding energies. Total energies of atoms, molecules, and solids are ordinarily quite accurate, but when electrons are removed or shifted from one level to another the eigenvalues do not by themselves give an accurate account of the change in energy. The well-known, but quite complex, GW method[2] appears to surmount this problem, but it requires going outside conventional density-functional theory. Godby, Schluter, and Sham[3] have concluded that density-functional theory by itself is unable to calculate excitation energies across a band gap without the addition of a discontinuous term in the exchange-correlation potential.

Slater has studied the role of eigenvalues in representing excited-state energies in atoms and molecules and found that self-consistent field calculations for a nonphysical state halfway between the ground state and an excited state were useful in calculating excitation energies. What he did is outside the scope of conventional density-functional theory, but from a calculational point of view is almost the same as the familiar local-density approximation. It is our goal to extend Slater's methods to band-structure calculations of insulators and semiconductors.

Slater[4] expanded the total energy in a Taylor series in the orbital occupations:

$$E(n_i) = \bar{E} + \sum_i \bar{E}_i(n_i - \bar{n}_i)$$
$$+ \frac{1}{2}\sum_i \sum_j \bar{E}_{ij}(n_i - \bar{n}_i)(n_j - \bar{n}_j) + \cdots. \quad (1)$$

$\bar{E}$ is the total energy when the occupations are $n_i = \bar{n}_i$; the $\bar{E}_i$ are the first derivatives of the total energy and are, as is well known, equal to the eigenvalues of the one-electron equations; and the $\bar{E}_{ij}$ are the second derivatives. The total energy of a second configuration n_i' is given by the same Taylor series. If one is interested in the difference in total energy between configurations n_i and n_i' the result is much simplified if one does a self-consistent field calculation with

$$\bar{n}_i = (n_i + n_i')/2. \quad (2)$$

This is Slater's transition state, and the result is easily seen to be

$$E(n_i') - E(n_i) = \sum_i \bar{E}_i(n_i' - n_i) + \text{third-order terms. } (3)$$

The second-order terms cancel out, and the excitation energy is obtained with good accuracy from the eigenvalue of the state halfway between the two configurations.

An example of the use of Slater's transition-state method is a calculation by Zangwill and Liberman[5] of the photoabsorption in xenon near the $3d$ edge. It is interesting that not only is the threshold for absorption located more accurately than in a conventional ground-state calculation, but the calculated cross section is better, showing that the orbital functions are better for the purpose of computing the transition matrix elements.

Application of the transition-state method to solids is ordinarily not considered, because removing the charge associated with half of an electron means removing charge represented by a delocalized Bloch function, which produces a negligible change in the charge density and thus in the potential function and the eigenvalues. Slater pointed out that a better physical picture for excitation in insulators and semiconductors is a localized hole. This idea has been implemented by specifying a simple model for the hole: it is confined to one cell of the solid's lattice. Further, since we are interested in band gaps, it is assumed that the charge is removed from the top of the valence band in one cell and put into a delocalized state at the bottom of the conduction band. Since the conduction-band electron is distributed over the entire volume of the solid, it contributes negligibly to the charge density and can be ignored. The final element in the transition-state model is the assumption that the orbital functions from which the charge density is constructed are Bloch functions and have the appropriate boundary conditions, so that a standard band-structure method may be used for their calculation.

This transition-state model of solids can be given a local-density formulation in the following way. Two density functions are defined: a Fermi density function

$$n_F(\mathbf{r}) = \sum_{\epsilon_{\mathbf{k}} < \epsilon_F} |\psi_{\mathbf{k}}(\mathbf{r})|^2 \qquad (4)$$

and a Slater density function

$$n_S(\mathbf{r}) = \sum_{\epsilon_{\mathbf{k}} < \epsilon_S} |\psi_{\mathbf{k}}(\mathbf{r})|^2, \qquad (5)$$

where the integrals of $n_F(\mathbf{r})$ and $n_S(\mathbf{r})$ in one unit cell are

$$\int_{C_0} n_F(\mathbf{r}) d\mathbf{r} = N \qquad (6)$$

and

$$\int_{C_0} n_S(\mathbf{r}) d\mathbf{r} = N - \tfrac{1}{2}. \qquad (7)$$

The orbital functions from which the density functions are constructed are Bloch waves. C_i is a cell of the solid labeled with the index i, and C_0 is the cell with the localized hole. The potential energy of the electrons in C_0 due to interactions with the atomic nuclei is

$$V[n_S] = -\sum_\alpha \int_{C_0} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} n_S(\mathbf{r}) d\mathbf{r}. \qquad (8)$$

The index α runs over all atomic nuclei in the solid. The electron-electron potential energy is

$$U[n_S] = \tfrac{1}{2} u_{00} + \sum_{i \neq 0} u_{0i}, \qquad (9)$$

where

$$u_{00} = \int_{C_0} \int_{C_0} \frac{n_S(\mathbf{r}) n_S(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} \qquad (10)$$

and

$$u_{0i} = \int_{C_0} \int_{C_i} \frac{n_S(\mathbf{r}) n_F(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}. \qquad (11)$$

In addition there is the local-density exchange-correlation potential energy

$$E_{\text{XC}}[n_S] = \int_{C_0} n_S(\mathbf{r}) \epsilon_{\text{XC}}(n_S(\mathbf{r})) d\mathbf{r}. \qquad (12)$$

The functional derivative of the potential energy with respect to $n_S(\mathbf{r})$ in the unit cell C_0 leads to the desired potential function,

$$v(\mathbf{r}) = -\sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} + \sum_{i \neq 0} \int_{C_i} \frac{n_F(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \int_{C_0} \frac{n_S(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$+ \frac{\partial}{\partial n_S(\mathbf{r})} [n_S(\mathbf{r}) \epsilon_{\text{XC}}(n_S(\mathbf{r}))]. \qquad (13)$$

$v(\mathbf{r})$ is the potential function in the cell C_0. The first term on the right is the Coulomb potential of the nuclei—both those inside C_0 and those outside. The second term is the Coulomb potential of the electronic charge outside C_0 and depends on $n_F(\mathbf{r})$. The third term is the Coulomb potential arising from the electronic charge inside C_0 which according to our assumptions depends on $n_S(\mathbf{r})$. And finally there is the exchange-correlation potential in C_0, which also depends on $n_S(\mathbf{r})$. The assumption made above that the one-electron wave functions are Bloch functions obeying Bloch boundary conditions implies that the potential functions in other cells, C_i, are the same as in C_0.

This potential function has been used in a linear muffin tin orbital (LMTO) computer program developed by Skriver.[6] In it the atomic-sphere approximation[7] with overlapping spheres is used. The calculations presented here all have two spheres containing atomic nuclei and two spheres without nuclei in each unit cell. The spheres are all the same size and their volumes add up to the unit-cell volume. Andersen's combined correction for overlapping spheres[7] was used.

Our calculations of band gaps are summarized in Table I. It is clear that at least in the cases listed there the transition-state model represents a substantial improvement over the conventional local-density ground-state calculations. The remaining differences between the experimental band gaps and the described here model come from various sources: (1) inaccuracies in some measured band gaps; (2) the arbitrarily chosen prescription for the localized hole; (3) approximations in the potential function associated with the atomic-sphere approximation; and (4) inaccuracies in the LMTO computer program especially in the conduction band.[10]

To summarize: a local-density-approximation band-structure model has been devised that is designed to give

TABLE I. Band gaps for several materials computed using the ordinary local-density approximation (LDA) and the transition-state model (TSM) with one-half electron removed from one unit cell. The experimental band gaps are from Ref. 8 (the semiconductors and MgO) and Ref. 9 (the alkali halides).

Material	Lattice constant (Å)	Gap type	E_g (LDA) (eV)	E_g (TSM) (eV)	E_g (expt) (eV)
Diamond structure					
C	3.560	indirect	4.18	5.33	5.50(5)
		direct	5.68	6.26	6.5
Si	5.431	indirect	0.49	1.31	1.1700
		direct	2.67	3.10	3.34–3.36
Zinc blende structure					
BN	3.615	indirect	4.45	6.85	6.4(5)
		direct	8.94	10.85	14.5
AlP	5.451	indirect	1.48	2.92	2.505(10)
		direct	3.15	4.05	3.63(2)
SiC	4.359	indirect	1.40	3.26	2.416(1)
		direct	6.6	7.5	6.0
Sodium chloride structure					
LiF	4.026	direct	8.97	13.83	14.5(5)
NaF	4.623	direct	6.24	11.53	11.5(5)
MgO	4.211	direct	4.94	8.12	7.833
NaCl	5.651	direct	4.67	9.20	9.0(5)

better estimates of band gaps in semiconductors and insulators than the conventional local-density calculation of the ground state. Its main features are a localized hole in one unit cell and the use of Slater's transition state, which tells us the hole is the result of removing the charge of half an electron from the top of the valence band.

Zunger and co-workers[11] have also used a transition-state model for solids. In their calculations a solid was assumed to be divided into ''supercells'' each comprising a number (up to 32) of atoms. In each supercell half an electron was removed from a core state and placed in the conduction band. A hole was created on a single atom or molecule and the half electron in the conduction band was more or less uniformly distributed over the supercell. Results of these calculations depend on the size of the supercell, beingbetter as it becomes larger and the half electron in the conduction band is spread out over a larger volume. In the model presented here, the half electron comes from a single cell and is spread out over the entire volume of the solid. This is closer to physical reality so far as the conduction band goes, but it ignores relaxation effects in the cells near the localized hole. The earlier work was concerned with core states and cannot be compared with our calculations of energy gaps between valence and conduction bands.

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[1] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[2] L. Hedin and S. Lundqvist, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.
[3] R. W. Godby, M. Schluter, and L. J. Sham, Phys. Rev. B 37, 10 159 (1988).
[4] J. C. Slater, Adv. Quantum Chem. 6, 1 (1972).
[5] A. Zangwill and D. A. Liberman, J. Phys. B 17, L253 (1984).
[6] H. L. Skriver, The LMTO Method (Springer-Verlag, Berlin, 1984).
[7] O. K. Andersen, Phys. Rev. B 12, 3060 (1975).
[8] Semiconductors—Basic Data, 2nd ed., edited by O. Madelung (Springer-Verlag, Berlin, 1996).
[9] R. Leckey, in Numerical Data and Functional Relationships in Science and Technology, edited by O. Madelung, Landolt-Bornstein, New Series, Group III, Vol. 23, Pt. a (Springer-Verlag, Berlin, 1989), p. 113.
[10] The accuracy of LMTO eigenvalues is discussed in Ref. 7. In the LMTO method the Γ point is singular. The energies in both the valence and conduction bands at this point were obtained from interpolations along the (100), (110), and (111) directions. In the valence band these three interpolations always gave energies close to one another. In the conduction band there was similar agreement among the three values for the materials listed in Table I, but for other materials with higher-Z components (Ge, ZnS, GaP, GaAs) the three estimates of the energy at the Γ point did not agree closely enough to get a reliable value.
[11] A. Zunger and A. J. Freeman, Phys. Lett. 60A, 456 (1977); Phys. Rev. B 16, 2901 (1977); S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B 52, 13 975 (1995).