PHYSICAL REVIEW B VOLUME 38, NUMBER 2 15 JULY 1988-I

Quantum-mechanical cluster-lattice interaction in crystal simulation: Many-body effects

A. Barry Kunz and Jie Meng
Department of Physics, Michigan Technological University, Houghton, Michigan 49931

John M. Vail
Department of Physics, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

(Received 7 January 1988)

The problem of describing quantum mechanically a region of interest in an otherwise extended lattice is discussed for nonmetallic solids. Hartree-Fock effects were considered in the preceding work, and in the present paper we consider the application of a many-body perturbation-theory correlation correction. The application of this formalism to NaF crystals containing Cu is considered as an illustration of the method. These results tend to validate the total procedure including the utility of correlation corrections for such problems.

I. INTRODUCTION

Lattice defects in crystalline materials, often in combinations that are difficult to resolve experimentally, determine many technologically important properties. Reliable computer simulation of such defects is therefore of potential value, and can be expected to contribute to fundamental understanding of the physical processes that determine the structure and properties of these materials. For point defects, an attractive approach is to use quantum mechanics to describe the response of the region near the defect to the defect and to embed this region in a potential similar to that of a perfect lattice. How this is accomplished is described in the preceding paper, as is lattice response. Here we show how the Hartree-Fock approach may be improved by using simple many-body-perturbation theory (MBPT). The use of this method is briefly illustrated for the case of NaF with a Cu impurity. This case also demonstrates the usefulness of MBPT in obtaining quantitatively useful results.

II. CORRELATION CORRECTIONS

In the preceding paper,[1] a prescription for obtaining the Hartree-Fock solution for a defect structure in the presence of a self-consistently relaxing lattice has been given. The use of the Hartree-Fock approach mentioned above for obtaining energy-band results has been seen highly inaccurate for both alkali halides and also rare gases since at least 1970.[2] One needs to account for correlation effects if quantitative accuracy is to be achieved. It is known that correlation effects consist of three principal parts:[3] electron-electron dynamic correlation, orbital relaxation, and electron-hole attraction effects. The state-by-state self-consistent Hartree-Fock method employed by us and described previously directly incorporate the two lattice effects. Therefore one need only incorporate the electron-electron dynamic correlation effect. This effect is well known to be significant even for tightly bound calculations, and can alter excitation energies by several eV at times.[4]

Correlation methods acceptable for solid-state calculations of total energy are constrained to be size consistent.[5] The statement that a correlation method must be size consistent simply implies that if one were to consider a homogeneous system containing a large number N of similar building block units, the total energy of this system would be directly and linearly proportional to N. This property is also termed extensive. In a formal many-body sense an extensive (size-consistent) approach is one which obeys the link-cluster theorem.[5]

There are many approximation methods available today which violate the concept of extensivity. A classic example described in detail by Thouless[5] is the use of Brillouin-Wigner perturbation theory to describe the ground state of a homogeneous many-body system. To the second order in Brillouin-Wigner theory the energy of the ground state, E_0, is given as

$$E_0 = W_0 + V_{00} + \sum_{i(\neq 0)} \frac{V_{i0}V_{0i}}{E_0 - W_i} . \tag{2.1}$$

Here, V_{i0} is the matrix element of the perturbation and W_i is the eigenvalue of state i of the unperturbed Hamiltonian. The presence of the unknown energy, E_0, in the denominator is responsible for the violation of extensivity in the use of Brillouin-Wigner perturbation theory. If however, one approximates the E_0 in the denominator with its zero-order value, W_0, one obtains

$$E_0 = W_0 + V_{00} + \sum_{i(\neq 0)} \frac{V_{i0}V_{0i}}{W_0 - W_i} . \tag{2.2}$$

This is recognized at once as the usual second-order Rayleigh-Schrödinger perturbation result. Interestingly enough, this result is extensive and development of perturbation methods along such lines, as we do later in this section, is also extensive and often termed MBPT.

It has been shown by Davidson and Silver[5] that incomplete configuration-interaction (CI) calculations are also not size consistent. In particular, Davidson and Silver consider a system of N dilute helium atoms forming a gas. They consider a CI calculation in which all double excitations of the ground state are considered. They obtain the result that the Hartree-Fock part of the energy of such a system is linearly proportional to N, and that the correlation part of the energy is directly proportional to $N^{1/2}$. This latter result is clearly incorrect in that it implies for a large system that the energy per atom is simply the Hartree-Fock energy of the atom, which is clearly wrong. Therefore in the interest of obtaining correct total-energy expressions, which is the principal product of the approach we employ, we are constrained to use one of the several available extensive methods.

Instead, one may choose a method based on MBPT.[5,6] In the normal single-reference application that is appropriate here, one divides the many-electron Hamiltonian H into two parts, namely a zero-order Hamiltonian H_0 whose eigenvalues and eigenfunctions are known, and a perturbation V:

$$H=H_0+V \ . \tag{2.3}$$

Usually H_0 would be chosen to be the sum of one-electron Fock operators,[2,6] but that is not convenient here. Rather, we pick H_0 to be the sum of the one-electron localized-orbital (modified Fock) operators from Eq. (2.15) from the preceding paper,

$$H_0=\sum_{i=1}^{N_A}[F_A(\underline{r}_i)+V_A^M+V_A^S-(\rho_A V_A^S \rho_A)\underline{r}_i] \ , \tag{2.4}$$

where ρ_A is defined in Eq. (2.9) of the preceding paper.

Now from having solved the local-orbital equation, we know the zero-order eigenvalue and eigenfunction of H_0, Eq. (2.4),

$$H_0\Phi_I=E_{I0}\Phi_I \ , \tag{2.5}$$

namely

$$E_{I0}=\sum_{k=1}^{N_A}\pi_k \ , \tag{2.6}$$

and Φ_I is the Slater determinant constructed out of the occupied single-particle orbitals $|\,k\,\rangle$ from the modified Fock equation. We now estimate the corresponding eigenvalue and eigenfunction of the full Hamiltonian H:

$$H\Psi_I=E_I\Psi_I \ . \tag{2.7}$$

Formally,

$$\Psi_I=[1-(H_0-E_{I0})^{-1}(1-p_I)(E_I-V-E_{I0})]^{-1}\Phi_I \ , \tag{2.8}$$

where p_I is the projection operator onto the state Φ_I. If size consistency is maintained, this leads to the perturbation series:

$$E_I=E_{I0}+\langle\Phi_I\,|\,V\,|\,\Phi_I\rangle + \langle\Phi_I\,|\,V(H_0-E_{I0})^{-1}(1-p_I)(-V)\,|\,\Phi_I\rangle+\cdots \ . \tag{2.9}$$

It follows that, to second order,

$$E_I=(E_{I0}+V_{II})+\sum_{J=I}V_{IJ}V_{JI}(E_{I0}-E_{J0})^{-1} \ , \tag{2.10}$$

where

$$V_{IJ}=\langle\Phi_I\,|\,V\,|\,\Phi_J\rangle \ . \tag{2.11}$$

The energy E_I can now be evaluated from Eq. (2.10) by noting that since

$$V=(H-H_0) \ , \tag{2.12}$$

it therefore follows from Eq. (2.4) that

$$E_{I0}+V_{II}=\langle\Phi_I\,|\,H\,|\,\Phi_I\rangle=\overline{E}_I \ , \tag{2.13}$$

where the energy $\overline{E}_I$, the expectation value of the whole Hamiltonian H with respect to state Φ_I, has already been evaluated, Eq. (3.3). Furthermore, from Eq. (2.12),

$$V_{IJ}=\langle\Phi_I\,|\,H\,|\,\Phi_J\rangle \ , \quad I\neq J \tag{2.14}$$

again having used Eq. (2.5), and the fact that Φ_I and Φ_J are orthogonal. The only nonzero matrix elements V_{IJ}, from Eq. (2.14), are those for which Φ_J differs from Φ_I by two—and only two—of its single-particle orbitals. This is a result of Brillouin's theorem, and the fact that H contains only one- and two-particle operators. If Φ_J differs from Φ_I by having orbitals $|\,i\,\rangle$ and $|\,j\,\rangle$ in Φ_I replaced by $|\,a\,\rangle$ and $|\,b\,\rangle$ in Φ_J, then

$$V_{IJ}=\langle ij\,|\,g(1-P)\,|\,ab\,\rangle \ , \tag{2.15}$$

where $g=2\,|\,\mathbf{r}-\mathbf{r}'\,|^{-1}$ and P is the pairwise interchange operator. Furthermore, in this case

$$E_{I0}-E_{J0}=\pi_i+\pi_j-\pi_a-\pi_b \ . \tag{2.16}$$

We therefore obtain the final result:

$$E_I=\overline{E}_I+\sum_{\substack{i<j\\ (\mathrm{occ})}}\ \sum_{\substack{a<b\\ (\mathrm{virt})}}\frac{(g_{ijab}-g_{ijba})^2}{\pi_i+\pi_j-\pi_a-\pi_b} \ . \tag{2.17}$$

In Eq. (2.17) the double sum over $i<j$ includes occupied orbitals in Φ_I and that over $a<b$ includes virtual (not occupied) orbitals for Φ_J, the inequalities being required to avoid double counting of excited eigenstates Φ_J $(J=I)$.

III. SAMPLE RESULT, NaF:Cu AND CONCLUSIONS

We would like to give a brief exposition of a sample result. For a crystal of NaF with a Cu impurity, this result will indicate the level of accuracy or precision possible for a simple defect system at both the Hartree-Fock level and using MBPT. Furthermore, it will indicate the level to which permitting lattice rearrangement affects such a system. This is a preliminary discussion and a much fuller exposition of this system is in preparation for publication.[7]

In this calculation, the cluster consisted of the central Cu^+ ion and its surrounding six F^- ions. The remainder of the NaF lattice received a shell-model treatment. The shell-model parameters used for NaF were taken from Cattow *et al.*[8] These potentials are first used to determine the NaF perfect-crystal lattice constant. This is found to be 2.30 Å, which is in reasonable agreement with an experimental value of 2.32 Å.

The defect cluster contains a total of 88 electrons (44 of each spin). To describe these electrons a total of 82 basis functions of each spin were incorporated. In the basic calculation, many experimental parameters were obtained, but for the present purposes we concentrate on three items: the relaxation of the lattice about the Cu^+ ion, the crystal-field splitting of the Cu^+ $3d$ orbital, and the $3d^{10}$-to-$3d^9 4s$ excitation of the Cu^+ ion.

The ICECAP procedure computes the lattice positions of ions inside and outside the cluster self-consistently in the presence of the defect. In the case of NaF:Cu the Cu^+ ion is substitutional for a Na^+ ion. According to available standard references, the size of the Cu^+ ion is not well established, ranging from 0.53 to 0.97 Å, whereas that of Na^+ is well defined as 0.98 Å. Therefore we expect that the nearest-neighbor F^- ion will relax inward toward Cu^+, but by an uncertain amount. In this calculation we find the inward relaxation to be by 1.1%, a value more in accord with an ionic radius of 0.97 Å rather than one of 0.53 Å. The more distant shells relax by lesser amounts. This small relaxation may seem insignificant (it is almost certainly too small to be measured), but in terms of energetics it is not. Due to the ionic nature of the lattice, the potential at the Cu^+-ion site changes by 0.41 eV due to this relaxation. This charge will be seen as significant compared to the ultimate precision of the calculation.

The second parameter is the crystal-field splitting of the Cu $3d$ orbital in NaF. This splitting is due to the cubic field of the crystal and it is into a threefold Γ'_{25} level and a twofold Γ_{12} level. This has been measured by McClure and found to be 0.35 eV. McClure and his group have also computed this quantity using the discrete variational $X\alpha$ method (DVM),[9] and have found it to be 0.45 eV. Using our present methods we find the crystal-field splitting to be 0.31 eV at the Hartree-Fock level and also at the MBPT level. This is seen by us as reasonable agreement with experiment and somewhat better than the DVM-$X\alpha$ result as well. The error 0.04 eV is far smaller than the potential changes due to lattice relaxation. The present determination of the crystal-field splitting is obtained by computing the ionization energies of the Γ'_{25} and Γ_{12} levels by differences of total energy and thus taking the difference in ionization energy. The calculations are performed to an aggregate numerical precision of about 10^{-4} eV.

Finally, the excitation energy of the $Cu^+ 3d^{10}$-to-$3d^9 4s$ transition is computed. McClure and associates measure this energy to be 4.2 eV and compute it to be 3.6 eV using the DVM-$X\alpha$ model.[9] Using our present methods, one finds the excitation energy to be 3.70 eV in Hartree-Fock limit and 4.02 eV in the MBPT limit. Clearly, the present result is an improvement over prior nonempirical attempts and the MBPT result agrees quite well with experment (4% error).

We find no difficulty in concluding that the ICECAP lattice self-consistency is a feasible computation, and that even small relaxation—$\sim 1\%$—can be useful and significant in determining energies in ionic systems. We also find that correlation corrections represent a significant benefit in spectral energy determination. It is worth noting that the correlation calculation performed perturbatively here represents contributions of 10 909 801 configurations. The cost of such precision is not trivial. The computation for NaF:Cu reported here used several hundred hours of computer time on an FPS 164 scientific computer.

ACKNOWLEDGMENTS

This work was performed at Michigan Technological University, and one of us (J.M.V.) is grateful for the Physics Department's hospitality there. One of us (A.B.K.) acknowledges financial support from the U.S. Department of Energy (Office of Basic Energy Sciences) under Grant No. DE-FG02-85ER45224. J.M.V. acknowledges financial support from the Natural Sciences and Engineering Council (NSERC) of Canada and from the University of Manitoba Research Board.

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