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AB INITIO CALCULATION OF ELECTRON EXCITATION ENERGIES IN SOLIDS

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Abstract

Progress in the first-principles calculation of electron excitation energies in solids is discussed. Quasiparticle energies are computed by expanding the electron self energy to first order in the screened Coulomb interaction in the so-called GW approximation. The method has been applied to explain and predict the spectroscopic properties of a variety of systems. Several illustrative applications to semiconductors, materials under pressure, chemisorption, and point defects in solids are presented. A recent reformulation of the method employing mixed-space functions and imaginary time techniques is also discussed.

1. Introduction

Materials design using computer modeling and simulation requires a good theoretical understanding of the different properties of materials including both their ground-state and excited-state properties. The recent advent of a first-principles quasiparticle method[1] has allowed *ab initio* calculation of the spectroscopic properties of real materials. The method is based on an expansion of the electron self energy operator to first order in the dressed electron Green's function and the dynamically screened Coulomb interaction in Hedin's GW approximation[2]. A key factor in computing quasiparticle energies for real materials is the inclusion of local field effects in the screened Coulomb interaction. This approach has been employed to explain and to predict results from optical, photoemission, scanning tunneling, and other spectroscopic measurements for a variety of systems. Recent refinements on the method using mixed-space functions and imaginary time techniques has further improved its computational efficiency. The new formulation yields a very favorable scaling of computational effort with the number of atoms in a unit cell, allowing study of even more complex materials systems. We give here a short review of the method and present some selected examples to illustrate the general applicability of the approach.

2. Theoretical Method

It is the quasiparticle excitations which essentially determine the spectral features measured in experiments such as photoemission, optical, and scanning tunneling measurements. However, traditional band structure methods such as the Hartree-Fock and local density functional (LDA) methods, being based on ground-state theories, do not give direct excitation energies. (See Table 1.) In the first-principles quasiparticle approach, the energies and wavefunctions of the quasiparticle states are obtained by solving a Dyson equation[1,2]:

$$[T + V_{ext}(r) + V_H(r)]\psi(r) + \int dr' \, \Sigma(r,r';E^{qp})\psi(r') = E^{qp}\psi(r) \quad , \tag{1}$$

where T is the kinetic energy operator, V_{ext} the external potential due to the ions, V_H the average electrostatic Hartree potential, and Σ the electron self-energy operator, respectively. The self-energy operator Σ describes the many-electron effects. In general, Σ is nonlocal, energy-dependent, and nonHermitian with the imaginary part giving the lifetime of the quasiparticles.

The GW approximation[2] involves taking the self-energy operator Σ as the first-order term in a series expansion of the screened Coulomb interaction W and the dressed electron Green function G:

$$\Sigma(r,r';E) = \frac{i}{2\pi}\int d\omega\, e^{-i\delta\omega}\, G(r,r';E-\omega)W(r,r';\omega) \qquad (2)$$

where δ is a positive infinitesimal. Since the screened Coulomb interaction is much weaker than the bare one, this first order term is found to be sufficient. In applications to real materials, the basic idea[1] is to make the best possible approximations for G and W, calculate Σ, and obtain the quasiparticle energies with no adjustable parameters. The screened Coulomb interaction $W=\varepsilon^{-1}V_C$ (where ε is the dielectric response function and V_C the bare Coulomb interaction) incorporates the dynamical many-body effects of the electrons. The dielectric response function $\varepsilon(r, r', \omega)$ is hence a crucial ingredient in determining the electron self energy. In a k-space formulation, the crystalline dielectric function is a matrix $\varepsilon_{GG'}(q,\omega)$ in the reciprocal lattice vectors. The off-diagonal elements of this matrix describe the local field effects which distinguish the variations in the electronic screening properties in different part of the crystal. These local fields are physically very important[3] and is a major component in the quantitative evaluation of the self-energy operator for a real material.

The k-ω space formulation of the GW method with local field effects has been applied quite successfully to the study of semiconductors and metals as well as surfaces, interfaces, clusters, point defects, and pressure induced insulator-metal transitions. These *ab initio* calculations are of particular value to the latter group of applications since these systems are often less well-characterized experimentally.

3. Selected Applications

Table 1 shows the calculated quasiparticle band gaps[1,4] of several prototypical semiconductors and insulators as compared to the LDA Kohn-Sham gaps and experimental values. The LDA gaps significantly underestimate the experimental values. On the other hand, with the excitation energies properly given as transitions between quasiparticle states, the calculated quasiparticle gaps are in excellent agreement with experiment. These results were obtained with only input being the atomic number of the constituent elements and the crystal lattice parameters. The use of a self-consistent crystal Green function and the inclusion of local fields (the full dielectric matrix) and dynamical screening effects are all shown to be key factors in describing accurately the self-energy effects. In general, the calculated optical transition energies (neglecting excitonic effects) are also within about 0.1-0.2 eV of the observed spectral features in optical measurements.

A comparison of the calculated quasiparticle band structure of Ge with data from angle-resolved photoemission and inverse photoemission measurements[5] is depicted in Figure 1. The agreement between theory and experiment is well within the experimental and theoretical error bars. The calculated unoccupied conduction band states for Ge were in fact predictions of the theory. The GW method has been applied, with equally impressive results, to numerous other semiconductors and s-p metals including materials as complex as solid C_{60}[6]. Figure 2 shows the theoretical density of states of solid C_{60}

Table 1. Comparison of calculated band gaps (in eV) with experiment. Core polarization and relaxation effects are included for Ge, AlAs, and GaAs.

	LDA	GW	Expt.[a]
diamond	3.9	5.6	5.48
Si	0.5	1.16	1.17
Ge	-0.26	0.73	0.74
GaAs	0.12	1.42	1.52
AlAs	1.28	2.01	2.24
LiCl	6.0	9.1	9.4

[a] See Refs. 1 and 4.

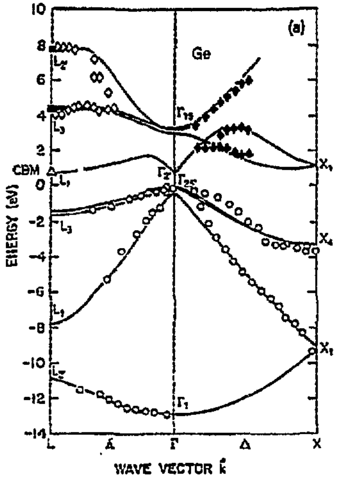

Fig. 1 Calculated quasiparticle energy of Ge compared to photoemission experiment [5].

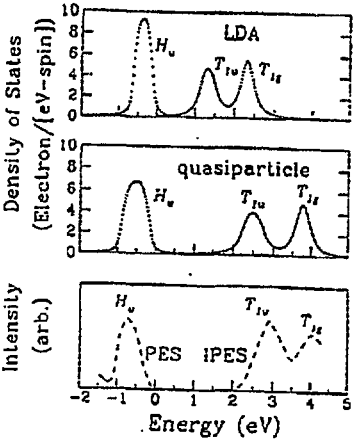

Fig. 2 Density of states of solid C60 based on LDA results, quasiparticle results and experimental data (see Ref. 6).

as compared to photoemission and inverse photoemission data. Recently, GW calculations have also been extended to the transition metal systems Ni and NiO [7].

Another useful application of quasiparticle energy calculations has been in studying the electronic properties of solids under pressure, in particular insulator-metal transitions. We discuss here the example of xenon under pressure. Solid Xe undergoes a pressure-induced isostructural insulator-metal transition, and the crystal structure is experimentally known to be hcp in the vicinity of the metallization pressure of 132(±5) GPa [8]. Our quasiparticle calculations [9] yielded a band gap closure at the pressure of 128 GPa, in good agreement with experiment. Figure 3 compares the theoretical band gaps as function of density with the values from optical measurements [8]. The quasiparticle results reproduce very accurately the volume dependence of the band gap, whereas the LDA results significantly underestimated the transition volume. The calculated quasiparticle bands further quantitatively explain all the salient features observed in the experimental optical spectra at metallization, in particular the appearance of a peak at ~2 eV in the absorption spectra which has been interpreted as electronic transitions to hole states at the top of the valence band made available when the conduction band overlaps the valence band. Another interesting finding is that the self-energy correction to the LDA band gap is not constant as a function of density. Thus it would not be possible to deduce the correct insulator-metal transition pressure from knowing just the pressure coefficient of the gap at low pressure and the LDA results.

The quasiparticle approach has been employed quite widely to analyze excitation spectra of semiconductor surfaces and band offsets at heterojunctions[10]. Here we briefly discuss

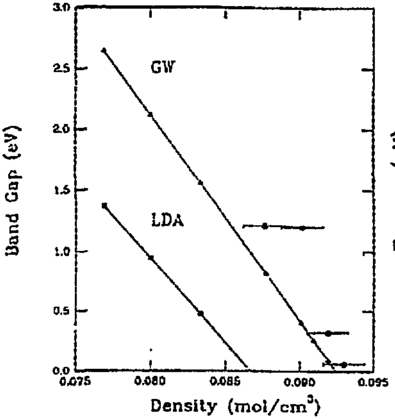

Fig. 3 LDA and GW band gap of hcp Xe as a function of density. Experimental data are the solid circles. (After Ref. 9.)

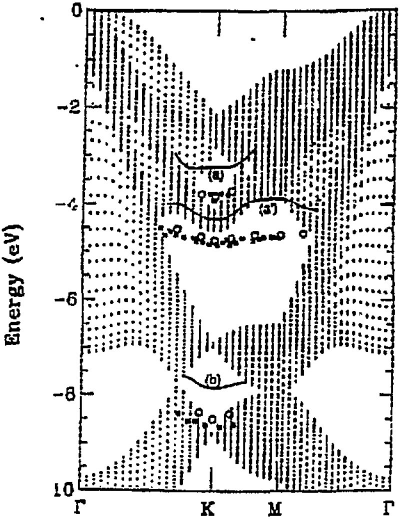

Fig. 4 Surface state bands of H/Si(111): LDA (full lines) and GW (open circles). Photoemission data are the black dots[11].

hydrogen on the Si(111) surface as a prototypical chemisorption system. This system has received considerable interest because of the development of a chemical method for preparing hydrogen terminated Si(111) surfaces which are highly stable, easily transportable, and structurally perfect over large areas. The calculations [11,12] were carried out using a surface geometry determined from LDA total energy minimization. Figure 4 depicts the calculated quasiparticle surface-state bands as compared to those from a LDA calculation as well as the measured surface-state energies from photoemission [11]. Two striking features may be seen from the figure. First, the shifts in the surface-state energies due to self-energy corrections are as much as 1 eV. These large self-energy effects are related to the very localized hydrogen 1s orbital forming the surface states. Second, the self-energy corrections to the LDA surface bands give rise to also a large change in the band dispersion, in particular, for the surface band (a'). These discrepancies are completely eliminated in the quasiparticle results. Analysis of the theoretical results showed that the large change in dispersion arises from the sensitivity of the nonlocal self-energy operator to the localization of the electron wavefunction [12]. The wavefunction of the surface state (a') at M is much more localized than that at K leading to a significantly larger self-energy correction for states near M.

As an example of GW quasiparticle calculations for point defects in solids, a study of the electronic excitation energies of a Cl vacancy or F-center defect in a LiCl crystal was carried out

[13]. Experimentally, these halogen vacancies, known as color centers for the visible coloration they induce [14], can be created by x-ray irradiation or by heating in an alkali vapor. The neutral vacancy contains a single bound electron, and the fundamental transition between the defect states give rise to absorption of visible light in the otherwise colorless salt. The theoretical electronic excitation results are summarized in Table 2 together with those from experiment and from LDA calculations. The quasiparticle energies of the bulk LiCl bands, e.g. the band gap in Table 2, are in good agreement with experiment. The additional single-particle excitations arising from transitions from the ground-state (1s level) of the F-center to the LiCl band continuum are found to be similarly accurate. Excitation energies corresponding to transitions to the conduction states at L, Λ and X are twice as large as those predicted by LDA. For the bound 1s→2p intrasite excitation, electron-hole interaction correction [13] needs to be included on top of the quasiparticle excitation transition energy. The resulting energy is 3.4 eV. This is in good agreement with the experimental values of 3.1-3.3 eV, and is in marked contrast with the LDA prediction of 2.4 eV.

Table 2. Bulk band gap and F-center defect excitation energies in LiCl compared to experiment (in eV). (After Ref. 13)

	LDA	GW	Expt.
Band gap	6.06	9.26	9.4
$1s \rightarrow 2p$	2.4	3.4	3.1 - 3.3
$1s \rightarrow L_C$	1.8	4.5	4.5
$1s \rightarrow \Lambda_C$	2.2	5.0	5.0
$1s \rightarrow X_C$	2.8	5.7	5.8

4. Some Recent Theoretical Developments

Although the method described in Section 2 is very robust, it is computationally demanding. In the k-ω space formulation, the computation effort scales as N^4 where N is the number of atoms in the unit cell. Previous applications have been mostly limited to $N<100$. Recent efforts [15-17] toward reformulating the method have resulted in some significant progress.

The most computationally intensive part of a self-energy calculation in the GW approximation is the evaluation of the independent electron polarizability χ^0. In the new formulation, χ^0 and other quantities including the Green's function and self-energy operator are calculated by introducing "mixed-space" functions [15] and imaginary time [16,17] techniques. In contrast to their real space analogs, the mixed-space functions have the full translational periodicity of the crystal. In use of these functions, the entire space can be rigorously folded into a single Wigner Seitz cell. This mixed-space approach is a considerable advantage over standard real space methods since in general two-points functions of crystals are non periodic in real space and have decay lengths which are significantly larger than a single unit cell. Unlike direct calculation in ω space, the use of the imaginary time techniques decouples the summation over the valence and conduction bands and damps the contributions of the higher conduction bands for insulators. The appropriate quantities of physical interest are then obtained using various fast Fourier transform and analytic continuation schemes, leading to a N^2 scaling for the most time consuming parts of a quasiparticle calculation.

The mixed-space imaginary-time formalism is shown to be very efficient for complex systems. It is particularly advantageous when the unit cell contains large vacuum regions such as in cases of surfaces, tubules, porous materials, molecules and clusters, because part of the grid can be neglected in the real-space integration. For example, compared to the k-space scheme, the crossover system size is as small as two atoms per cell in the case of bulk silicon.