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## Materials Sciences Division

Presented at the Quantum Theory of Real Materials Conference, Berkeley, CA, August 13, 1994, and to be published as a chapter in *Quantum Theory of Real Materials*

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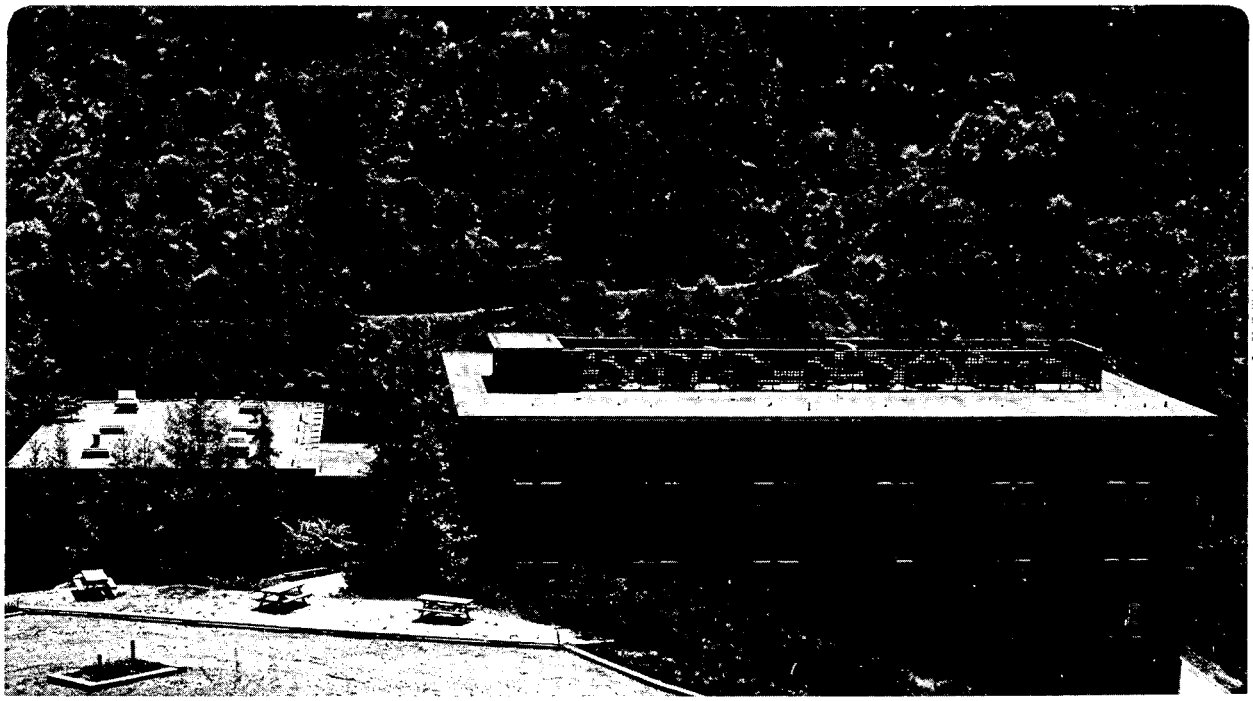
October 1995



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This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by the National Science Foundation under Grant No. DMR95-20554.

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To appear as a chapter in "Quantum Theory of Real Materials", eds. J.R. Chelikowsky and S.G. Louie, Kluwer Press.

# QUASIPARTICLE THEORY OF ELECTRON EXCITATIONS IN SOLIDS

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## Abstract

*A first-principles quasiparticle approach to electron excitation energies in solids is reviewed. The theory has been applied to explain and predict the spectroscopic properties of a variety of systems including bulk crystals, surfaces, interfaces, clusters, defects, and materials under pressure. Several illustrative applications are presented and some recent theoretical developments discussed.*

## 1. INTRODUCTION

In the 1960's, the Empirical Pseudopotential Method developed by Marvin L. Cohen and his collaborators [1] provided a theoretical means based on a few experimentally determined parameters to unravel the electronic structure and optical properties of semiconductors. Subsequent development of the *ab initio* pseudopotential total energy methods [2,3] in the 1980's allowed a first-principles determination of the structural, vibrational, and related ground-state properties of

solids. The introduction of the *ab initio* molecular dynamics approach [4] further made possible the evaluation of dynamical and thermodynamical quantities. A parallel and complementary development has been the advent of a first-principles method for the electron (quasiparticle) excitation energies [5]. Similar to the *ab initio* total energy methods for ground-state properties, the quasiparticle approach permits the computation and prediction of the excited-state properties of real materials from first principles.

Because of many-electron effects [6], the electron excitation spectra of solids can be significantly different from those of an independent-electron picture. The first-principles quasiparticle method [5], developed in the mid 1980's, incorporates these effects into the self energy of the electrons and has shown to yield very accurate excitation energies for real materials. It thus provides an important theoretical link between structural studies and spectroscopic probes. 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 [7]. A key ingredient for real materials is the inclusion of local field effects in the dielectric response. *Ab initio* calculations using this approach have been applied to understand and predict results from optical, direct and inverse photoemission, scanning tunneling, and other spectroscopic measurements for a variety of systems. In this article, we give a short discussion of the method and present some selected applications to semiconductors, materials under pressure, chemisorption, and point defects to illustrate the approach.

The remainder of the article is organized as follows. The theoretical formulation is briefly reviewed in Section 2. Results for several prototype systems including bulk crystals, solid xenon and molecular hydrogen under pressure, the H/Si(111) surface, and a color center in LiCl are presented in Section 3. Section 4 discusses some recent refinements of the method. Finally, Section 5 gives a summary and conclusions.

## 2. FIRST-PRINCIPLES CALCULATION OF QUASI-PARTICLE EXCITATIONS

Although *ab initio* electronic structure methods based on the local density approximation (LDA) generally yield very accurate results for structural energy and related properties of solids, these methods, being based on a ground-state theory, do not directly give electron excitation energies. For example, the use of LDA Kohn-Sham eigenvalues for interpreting spectroscopic data had often led to rather severe discrepancies. The LDA calculations incorrectly predicted Ge to be a metal and gave Si a band gap of 0.5 eV instead of the experimental value of 1.17 eV. In general, the band gaps of semiconductors and insulators are underestimated in the LDA by 50-100%, and Hartree-Fock (HF) results are usually several times too large compared to

experiment. Similar problems exist for any excitation spectra of solids which involve promoting an electron away from the ground state. In some cases, LDA calculations even give incorrect band orderings and band dispersions.

A quantitative description of spectroscopic data of solids requires knowing the properties of quasiparticles, i.e., the particle-like excitations in an interacting many-electron system [6]. It is the quasiparticle excitations which essentially determine the spectral features measured in experiments such as photoemission, optical, and scanning tunneling measurements. However, because of the complexity of the strong electron-electron interactions in solids, it remained a major challenge to calculate the quasiparticle energies of real materials from first principles. Considerable theoretical efforts had been devoted to this problem since the 1950's.

In the first-principles quasiparticle approach, the energies and wavefunctions of the quasiparticle excited states are obtained by solving a Dyson equation [5, 6]:

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

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

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

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

where $\delta$ is a positive infinitesimal. One makes use of the fact that the screened Coulomb interaction is much weaker and hence would lead to a rapid convergent series. In applications to real materials, the basic idea [5] is to make the best possible approximations for G and W, calculate $\Sigma$, and obtain the quasiparticle energies without any adjustable parameters. The screened coulomb interaction $W = \varepsilon^{-1}V_c$ (where $\varepsilon$ is the dielectric response function and $V_c$ the bare Coulomb interaction) incorporates the dynamical many-body effects of the electrons. Hence the dielectric response function $\varepsilon(\mathbf{r}, \mathbf{r}',\omega)$ is a key ingredient in determining the electron self energy. In a k-space formulation, the crystalline dielectric function is a matrix $\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$ 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 [8] and is a major component in the quantitative evaluation of the self-energy operator for a real material. A crucial factor that made possible the first *ab initio* calculation of quasiparticle energies in semiconductors had been the development of techniques for calculating the static dielectric matrices together with a scheme for extending them to finite frequencies.

In principle, the quasiparticle energies $E_{qp}$ and wavefunction $\psi$ which enter the electron Green's function G need to be calculated self-consistently with $\Sigma$ and G. In practice, G is constructed using the LDA Kohn-Sham eigenvalues and wavefunctions and iteratively updated with the quasiparticle spectrum from Eq. (1). The quasiparticle wavefunctions have been shown to be virtually identical to the LDA eigenfunctions in many cases. For most calculations, the dynamical dielectric matrix is typically obtained in a two-step process. The static dielectric matrix is first computed as a ground-state property within the LDA. Each element of the static dielectric matrix is then extended to finite frequencies using a generalized plasmon pole model employing exact dispersion and sum rule relations [5]. There are no adjustable parameters in this procedure. (For some cases, a model static dielectric matrix can be used, resulting in a significant computation saving without losing accuracy.) Comparison with results from calculations using alternative methods [9] to compute the $\omega$ dependence of $\varepsilon$ showed that the generalized plasmon pole scheme is very accurate in general for systems with s and p electrons.

The k-$\omega$ space formulation of the quasiparticle method 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. The parameter-free nature of the calculations is of particular importance to the latter group of applications since these systems are often less well-characterized experimentally. We present below some selected examples from these studies, and discuss some recent extensions of the approach which make use of mixed-space and imaginary time techniques with the potential of greatly simplifying the calculations.

# 3. SOME ILLUSTRATIVE APPLICATIONS

## 3.1 Band Gaps and Spectral Properties of Semiconductors and Insulators

Table 1 gives the calculated quasiparticle band gaps [5, 10] of several prototypical semiconductors as compared to the LDA Kohn-Sham gaps and experimental values. As discuss above, the LDA gaps significantly underestimate the experimental values. Table 1 shows that, with the excitation energies properly interpreted as transitions between quasiparticle states, the calculated gaps are now in excellent agreement with

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

| | LDA | Present Theory | 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. 5 and 10.

Table 2. Comparison between theory and experiment for optical transitions (in eV) in Ge, Si, and diamond. (After Ref. 5.)

| | LDA | Present work | Expt. |
|---|---|---|---|
| Ge | | | |
| $\Gamma_{7v} \rightarrow \Gamma_{8v}$ | 0.30 | 0.30 | 0.297 |
| $\Gamma_{8v} \rightarrow \Gamma_{7c}$ | −0.07 | 0.71 | 0.887 |
| $\Gamma_{8v} \rightarrow \Gamma_{6c}$ | 2.34 | 3.04 | 3.006 |
| $\Gamma_{8v} \rightarrow \Gamma_{8c}$ | 2.56 | 3.26 | 3.206 |
| $X_{5v} \rightarrow X_{5c}$ | 3.76 | 4.45 | 4.501 |
| Si | | | |
| $\Gamma_{25'v} \rightarrow \Gamma_{15c}$ | 2.57 | 3.35 | 3.4 |
| $\Gamma_{25'v} \rightarrow \Gamma_{2'c}$ | 3.26 | 4.08 | 4.2 |
| $L_{3'v} \rightarrow L_{1c}$ | 2.72 | 3.54 | 3.45 |
| $L_{3'v} \rightarrow L_{3c}$ | 4.58 | 5.51 | 5.50 |
| Diamond | | | |
| $\Gamma_{25'v} \rightarrow \Gamma_{15c}$ | 5.5 | 7.5 | 7.3 |
| $\Gamma_{25'v} \rightarrow \Gamma_{2'c}$ | 13.1 | 14.8 | 15.3±5 |
| $X_{4v} \rightarrow X_{1c}$ | 10.8 | 12.9 | 12.5 |

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 important factors in describing accurately the self-energy effects. *Ab initio* pseudopotentials are also typically used to facilitate the calculations. Thus, core-valence interactions [10] can sometimes affect the values of certain gaps in materials with very shallow and highly polarizable core states. In Table 1, the values for the minimum band gap of Ge, GaAs and AlAS were calculated with the core-polarization effects included. The change in the direct gap of GaAs is ~0.4 eV. The core-polarization effects on the gaps of the other materials listed in Table 1 are however typically about 0.1 eV or less.

In general, the calculated transition energies (neglecting excitonic effects) are within about 0.1-0.2 eV of the observed spectral features in optical measurements. This level of accuracy is comparable to empirical fitting methods. Table 2 presents

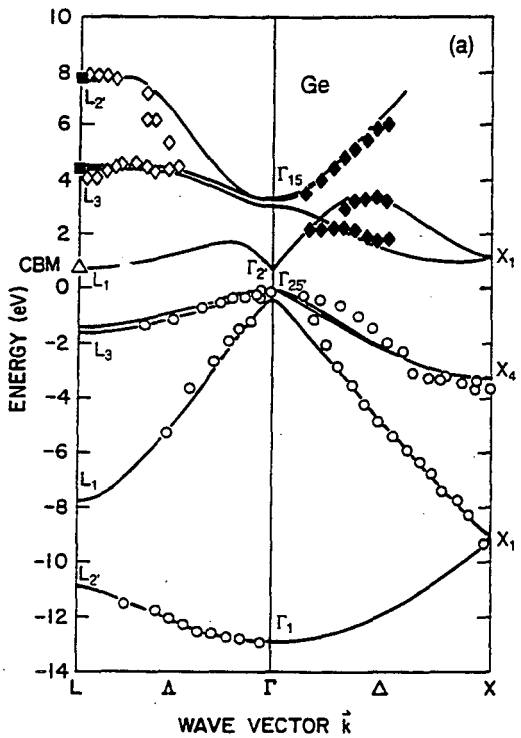


Fig. 1. Calculated quasiparticle energy of Ge compared to direct/inverse photoemission experiments [11, 12].

some of the optical results for Si, Ge and diamond. A comparison of the calculated quasiparticle band structure of Ge with data from angle-resolved photoemission [11] and inverse photoemission [12] measurements 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 solid $C_{60}$ [13] and the wide gap materials AlN and GaN [14]. Recently, GW calculations have also been extended to the transition metal systems, Ni [15] and NiO [16].

## 3.2 Materials under Pressure

Another useful application of quasiparticle energy calculations is in studying the electronic properties of solids under pressure, in particular insulator-metal transitions. We discuss three examples here: solid Xe, molecular solid hydrogen, and diamond.

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 [17, 18]. Our quasiparticle calculations [19,20]

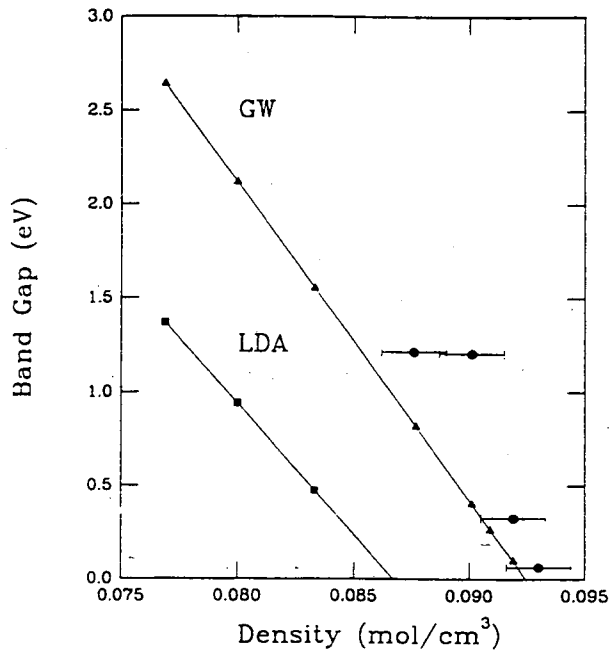


Fig. 2. LDA and GW minimum band gaps of hcp Xe as function of density. Experimental data from Ref. 17 are shown as solid circles.

yielded a band gap closure at the pressure of 128 GPa, in good agreement with experiment. Figure 2 compares the theoretical band gaps as function of density with the values from optical measurements [17]. The quasiparticle results reproduce very accurately the volume dependence of the band gap, whereas the LDA results significantly underestimated the transition volume. With spin-orbit interactions included, the calculated bands 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 after the band gap closed. Another important finding from the calculation is that the self-energy correction to the LDA band gap is not constant as a function of density. So it is not possible to deduce the insulator-metal transition from knowing just the pressure coefficient of the gap at low pressure and the LDA results.

A rapid change in the self-energy correction to the band gap as a function of density is also clearly seen in Fig. 3 for solid molecular hydrogen [20, 21]. The high

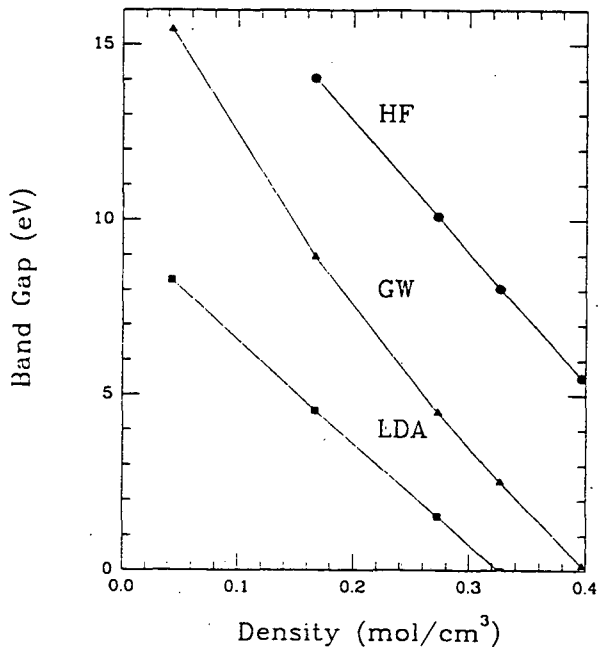


Fig. 3. Calculated GW, Hartree-Fock (HF) and LDA minimum gap of orientationally ordered solid molecular hydrogen in hcp structure as a function of density.

pressure phases of solid $H_2$ are more complicated because of the complex orientations possible for the hydrogen molecular axis and because of the large zero-point motions energy. Accurate structural determination remains a difficult task. We carried out calculations for $H_2$ in the hcp structure with the molecular axes either aligned along the c-axis or having different degrees of orientational disorder modeled within a crystal field approximation. In Fig. 3, the quasiparticle gaps are compared with those from Hartree-Fock (HF) and LDA calculations. In addition to the already mentioned problem of HF overestimating and LDA underestimating the gap, we find that both HF and LDA predict a linear behavior in the band gap versus density, whereas the quasiparticle results do not show such a linearity. This difference arises from a significant increase in the dielectric screening with density, which results in a strong and nontrivial dependence of the self-energy correction to the LDA band gap on density. Figure 4 depicts a comparison of theory with experimental measured gaps

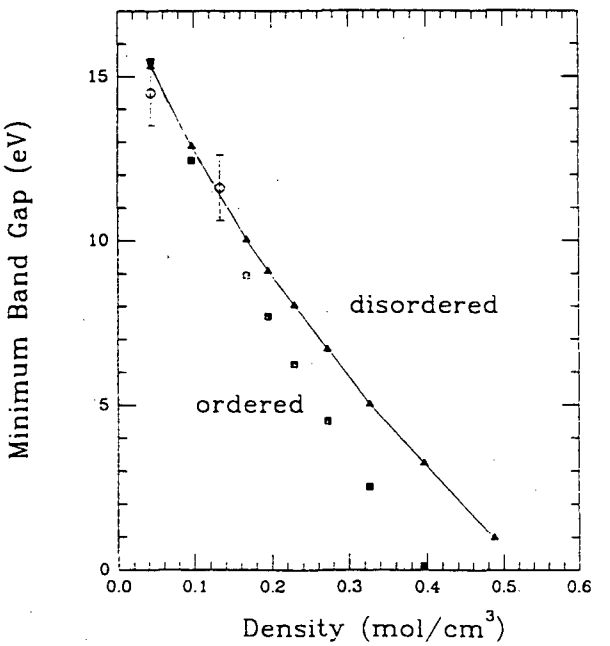


Fig. 4. Variation of the calculated quasiparticle band gap with density for the orientationally ordered and disordered phases of hcp molecular hydrogen. Experimental results are from Refs. 22 and 23.

[22,23] which shows again excellent agreement. At higher density, molecular orientational order however plays an increasingly important role in determining the value of the gap, preventing a definitive prediction of the pressure for band closure. For a given density, theory predicts that the minimum band gap increases monotonically and nonlinearly with orientational disorder.

Another system of particular interest and importance is diamond, owing to its role in pressure anvil cells. The changes in band gaps, dielectric screening, and electronic properties of diamond under stress have been calculated [24] using the quasiparticle approach. It is found that, contrary to the static pressure case, the minimum gap of diamond is significantly reduced under megabars uniaxial stress. However, the details of the electronic structure and the critical pressure for insulator-metal transition are sensitive to the exact stress profile in the crystal. These changes in the optical response of diamond under large stress are extremely relevant to the analysis of high pressure experiments, since diamond is employed both as containing walls and windows through which optical probes traverse.

## 3.3 H/Si(111) Surface

The quasiparticle approach has been employed quite widely to analyze excitation spectra of semiconductor surfaces and band offsets at heterojunctions. Examples of several applications can be found in the articles by M. Hybertsen and by J. Northrup in this Volume. Here we briefly discuss hydrogen on the Si(111) surface as a prototypical chemisorption system. This system has recently received considerable interest because of the development of a chemical method [25] for preparing hydrogen terminated Si(111) surfaces which are highly stable, easily transportable, and structurally perfect over large areas.

The calculations [26,27] were carried out using a surface geometry determined from total energy minimization in a 14-layer supercell geometry. Figure 5 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 [26]. Two striking features are seen from the figure. First, the shifts in the surface-state energies due to self-energy corrections are very large. The shifts are larger by a factor of 2 to 3 as compared to those on occupied surface states found in previously studied systems. The larger self-energy effects here 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 an unexpectedly large change in the band dispersion. In particular, the LDA surface band (a') in Fig. 5 shows a 0.42 eV dispersion going from K to M which disagrees with the near dispersionless data from photoemission. The discrepancy is completely eliminated in the quasiparticle results. Analysis of the theoretical results showed that this large change in dispersion arises from the sensitivity of the nonlocal self-energy operator to the localization of the electron

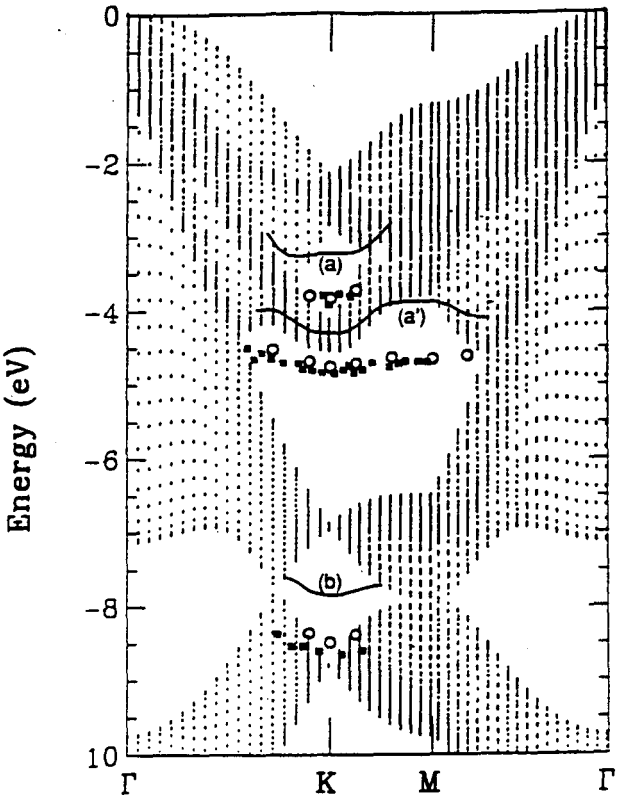


Fig. 5. Calculated surface-state bands of H/Si(111): LDA (full lines) and GW (open circles). The photoemission data (black dots) are from Ref. 26

wavefunction [27]. 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.

Studies of the above kind have demonstrated that very accurate quasiparticle energies may be obtained for semiconductor surfaces and interfaces. With the calculated electronic structure, one can then go on to study other phenomena such as surface electron-hole interactions in optical transitions [28]. It is found that self-energy effects can significantly change the position and band dispersion of both the occupied and empty surface states. As a result, the quasiparticle band gaps between occupied and empty surface states are typically much larger than the LDA Kohn-Sham values. Some of these changes are qualitatively similar to the self-energy corrections to the bulk-state energy gaps. However, the self-energy corrections to the surface

states are in general quite different from those to the bulk states [29]. The differences arise from changes in screening at the surface which lead to a change in the self-energy operator $\Sigma$ and from changes in the characters of the surface-state wavefunction which can be substantially different from those of the bulk states.

## 3.4 F-Center in LiCl

As an example of GW quasiparticle calculations for point defects in solids, a study of the electronic excitation energies of a F-center defect in a LiCl crystal was carried out [30]. The halogen vacancy constituting the F-center is modeled in a supercell consisting up to 54 atoms. Experimentally, these halogen vacancies, known as color centers for the visible coloration they induce [31], 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 Cl vacancy induces only a small lattice relaxation. The theoretical electronic excitation results [30] are summarized in Table 3 together with those from experiment [32-34] and from LDA calculations. The GW quasiparticle energies of the bulk LiCl

Table 3. Bulk band gap and F-center defect excitation energies in LiCl compared to experiment (in eV). (After Ref. 30)

| | LDA | GW | Expt. |
|---|---|---|---|
| Band gap | 6.06 | 9.26 | 9.4[a] |
| $1s \rightarrow 2p$ | 2.4 | 3.4 | 3.1 - 3.3[b] |
| $1s \rightarrow L_c$ | 1.8 | 4.5 | 4.5[c] |
| $1s \rightarrow \Lambda_c$ | 2.2 | 5.0 | 5.0[c] |
| $1s \rightarrow X_c$ | 2.8 | 5.7 | 5.8[c] |

[a]Ref. [32]
[b]Ref. [33]
[c]Ref. [34]

bands, e.g. the band gap in Table 3, are similar to those in previous crystalline calculations and are in good agreement with experiment [32]. 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. The 1s defect state is calculated to be at 4.0 eV below the conduction band minimum. Excitation

energies corresponding to transitions to the conduction states at L, $\Lambda$ and X are twice as large as those predicted by LDA and are in excellent agreement with experiment. For the bound 1s→ 2p intrasite excitation, electron-hole interaction correction [30] 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.

## 4. RECENT THEORETICAL DEVELOPMENTS

While the method described in Section 2 is very robust, it is computationally intensive. In the k-$\omega$ space formulation, the computation effort scales as $N^4$ where N is the number of atoms in the unit cell, and previous applications have been limited to N<100. Also, although the generalized plasmon pole model is very accurate for quasiparticle energies in sp electron systems, treatment of life-time effects and materials with d electron would require a faster and more accurate calculation of the dynamical screening. Recent efforts [35-37] toward improving the range of validity and computational efficiency of the GW method have resulted in some significant progress.

A major component of a self-energy calculation in the GW approximation is the evaluation of the independent electron polarizability $\chi^\circ$. In the new formulation, $\chi^\circ$ and other quantities including the Green's function and self-energy operator are calculated by introducing "mixed-space" functions [35] and imaginary time [36,37] 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. For example, $\chi^\circ$ is expressed as

$$\chi^\circ(\mathbf{r},\mathbf{r}',i\tau) = \sum_{\mathbf{q}} e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\, \chi^\circ_{\mathbf{q}}\, (\mathbf{r},\mathbf{r}',i\tau) \tag{3}$$

with

$$\chi^\circ_{\mathbf{q}}\, (\mathbf{r},\mathbf{r}',i\tau) = i \sum_{\mathbf{k}} G_{\mathbf{k}}\, (\mathbf{r},\mathbf{r}',i\tau)\, G_{\mathbf{k}+\mathbf{q}}\, (\mathbf{r},\mathbf{r}',-i\tau) \tag{4}$$

and the mixed-space Green's function in imagineray time now given by

$$G_{\mathbf{k}}(\mathbf{r},\mathbf{r}',i\tau) = \begin{cases} i \sum_{n}^{occ} U_{n\mathbf{k}}(\mathbf{r})\, U_{n\mathbf{k}}^{*}(\mathbf{r}')\, e^{-E_{n\mathbf{k}}\tau} & \tau \leq 0 \\ -i \sum_{n}^{unocc} U_{n\mathbf{k}}(\mathbf{r})\, U_{n\mathbf{k}}^{*}(\mathbf{r}')\, e^{-E_{n\mathbf{k}}\tau} & \tau > 0 \end{cases} \tag{5}$$

where U is the periodic part of the Bloch function. 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 energy or $\omega$ 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 especially in cases of large supercells. 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 grid can be skipped in the real-space integration. In fact, compared to the k-space scheme, the crossover system size is as small as two atoms per cell in the case of bulk silicon.

## 5. SUMMARY AND CONCLUSIONS

We have given a short review of a first-principles quasiparticle method based on the GW approximation for calculating electron excitation energies in solids and presented results from several selected applications. This quasiparticle approach has provided a general theoretical framework for computing accurate excitation energies from first principles for real materials, similar to that of the LDA for *ab initio* calculations of ground-state properties. Systems discussed here include bulk crystals, materials under pressure, hydrogen chemisorption, and a vacancy in LiCl. In all the cases, the theoretical results have given very accurate description of their spectroscopic properties as measured in photoemission, optical, and transport experiments. Besides the examples given here, the method has been successfully applied to a number of other systems including surfaces, interfaces, superlattices, and clusters. In general, accuracy at the level of 0.1 eV has been achieved for sp electron systems. Recent calculations on d-band materials have also yielded very encouraging results. The latest theoretical and algorithmic developments further show that a very favorable scaling of the method with the number of atoms in a cell can be achieved, allowing computation

of even more complex systems with perhaps hundreds or thousands of atoms in the future.

## ACKNOWLEDGMENTS

I would like to thank all my collaborators who contributed to the work reviewed here. This work was supported by NSF Grant No. DMR95-20554 and by the U.S. DOE under Contract No. DE-AC03-76SF00098. Supercomputer time was provided by the NSF San Diego Supercomputer Center, the NSF Pittsburgh Supercomputer Center, and by the National Energy Research Supercomputer Center.

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