

FIRST-PRINCIPLE CALCULATION OF SELF-ENERGY CORRECTIONS
IN COVALENT CRYSTALS

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A summary is presented of investigations performed on single-particle-like excitations in a covalent insulator. The self-energy is obtained replacing the Coulomb potential in the exchange operator by a dynamically screened interaction. At the same time, to be consistent with a variety of experimental facts, the dielectric function is taken in the time-dependent screened Hartree-Fock approximation. The correlated band structure is then derived from a local-orbital representation, utilizing in particular the short-range character of the self-energy. It is shown for the prototype diamond that the experimental band gap, the valence bandwidth, and the general features of quasi-particle decay observed in XPS can be reproduced by a first-principle calculation. Interrelations with the local-density concepts are discussed.

I. Introduction

A long-standing problem in calculating electronic excitations in solids has been the proper inclusion of many-particle effects. Efforts have been made in two directions. On the one hand, energy-band calculations have given a kind of pragmatic answer of how to include exchange and correlation effects on the single-particle-like excitations embedded in the one-particle Green's function. On the other hand, a large amount of work has been directed towards interaction effects embedded in the two-particle Green's functions [1], and specifically in the dielectric response function ϵ^{-1} . The main purpose of this work is to present a summary and discussion of recent first-principles investigations we have performed on the one-electron quasi-particle properties of strongly inhomogeneous crystals [2]. We demonstrate, in particular, that there exists a need to be as accurate as possible in the two-particle Green's function to get a satisfying description of the single-particle spectrum. We have performed such a first-principle calculation by the Green's functions method with a self-energy obtained by replacing the Coulomb potential in the (exchange) Hartree-Fock operator by a dynamically screened interaction. Diamond was chosen as prototype of

covalent materials. To be consistent with our results on the influence of many-particle effects in the optical absorption [1] and the impurity screening [3], we have taken the dielectric function of the medium within the time-dependent screened Hartree-Fock approximation. Previous calculations along similar lines have been restricted either to RPA frequency-independent and model dielectric functions or to a plasmon-pole approximation. We have investigated for the first time the role of a realistic frequency and wave-vector dependent dielectric function, and examined the relative importance of the electron-hole excitations and of the plasma resonance across the range of the valence and conduction bands. The correlated band structure was calculated in a local-orbital basis in order to exploit the local character of both the self-energy and the orbitals spanning these bands. We have found that the plasma resonance does not contribute appreciably in the energy range about the band gap (7.4 eV), thereby suggesting that a local-density approximation can be appropriate to describe the bands in this range. On the other hand, the plasma resonance was found to contribute significantly to the total valence bandwidth. Our value of 25.2 eV is in good agreement with photoemission data, whereas previous $X\alpha$ and LDA calculations have given about 20.5 eV. In addition, our method, by using an energy-dependent self-energy, has also enabled us to calculate quasi-particle damping times that are consistent with photoemission spectra.

II. Local-Orbital Description of Quasi-Particle States. Calculation for Diamond

We base our calculation of self-energy corrections in crystals with predominantly localized electronic character on a local-

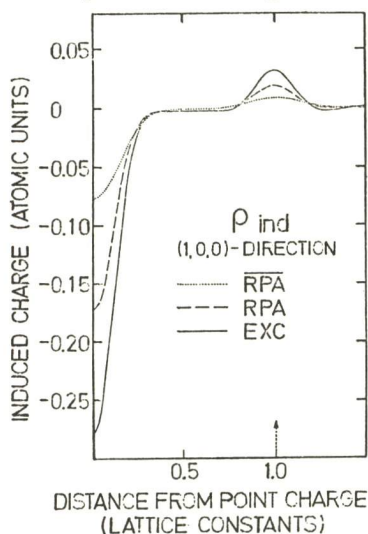


Fig.1: Impurity screening in diamond

induced by a substitutional impurity ($Z=1$) in diamond as shown in Fig. (1) along the (100) direction within the RPA without local-

orbitals description of the valence and low-lying conduction bands, the approach resting its validity on the short-range character of the self-energy operator [4]. The quasi-particle eigenvalue equation can thus be cast in the form of a non-hermitian algebraic eigenvalue problem whose complex solutions furnish both the energy and the spread of the excitation of a quasi-particle. According to the scheme developed by Hanke and Sham [1], the same local-orbitals basis is also used to calculate the inverse dielectric matrix that enters the dynamically screened interaction in the self-energy operator. This scheme enables us to go beyond the commonly used RPA approximation and include the excitonic (EXC) effects which are expected to be important in an accurate description of the short-range correlation hole about each electron. To get a direct feeling for this effect, we can compare the charge density

field effects ($\overline{\text{RPA}}$), the full RPA, and the EXC approximation [3].

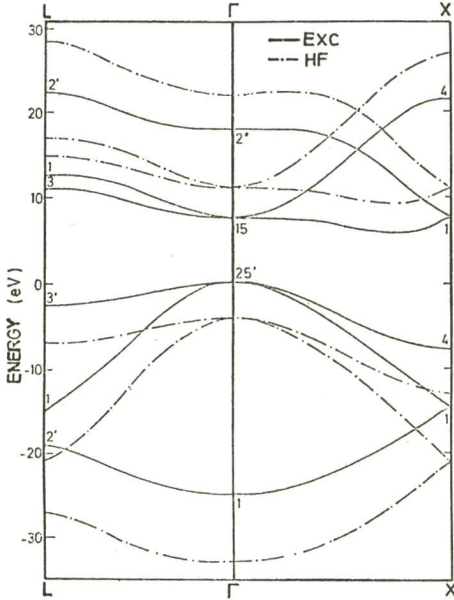


Fig.2: Quasi-particle band-structure (diamond)

Fig.(2) shows the quasi-particle band structure for diamond along two symmetry directions with the screening taken within the EXC approximation (full line) as compared to the Hartree-Fock band structure (dash-dotted line). The value of the optical gap and the valence bandwidth are compared with the experimental values in Table I. We notice a drastic reduction of the gap to 7.4 eV in agreement with the experimental value, and also a valence bandwidth reduction to 25.2 eV in close accord with XPS data.

We have performed an analogous calculation using the RPA dielectric function with the results that self-energy corrections come now to be generally smaller than in the EXC case. In particular, both the gap and the bandwidth increase by about 1 eV, thereby indicating that there

exists a need for an accurate description of the two-particle excitations to get accurate single-particle levels.

Table I: Quasi-particle energies (in eV)

	Exper.	HF ^(c)	EXC ^(d)	RPA ^(d)	E-H ^(d)	"COHSEX" ^(d)	LDA ^(e)
E_{gap}	7.3 ^(a)	15.	7.4	8.25	7.4	7.2	6.3
ΔE_{val}	24.2±1 ^(b)	29.	25.2	26.1	26.45	28.83	20.4

(a) Ref.5; (b) Ref.6; (c) Ref.7; (d) This work; (e) Ref. 8.

In order to extract explicitly the influence of the electron-hole and plasmon excitations to the self-energy corrections, we have performed an additional calculation where the plasmon contribution is cut off. The gap is found unchanged (7.4 eV) and, therefore, the properties of quasi-particles in the vicinity of the top of valence and bottom of conduction bands are entirely determined by coupling to the electron-hole excitations. Since the electron-hole correlation effects are predominantly of short-range character, we might conclude that correlation in the vicinity of the band gap can be accounted for by a "local" description, along the lines of the prescription given by Sham and Kohn [4]. The fact that the "ground state" LDA calculations give only 6.3 eV (cf. Table I) might, however, be due to the use of a local exchange-correlation operator which overestimates

the effect of screening over and above the Hartree-Fock approximation.

We have tested the so-called COHSEX approximation proposed by Hedin [9] where the screening properties of the medium are assumed to be essentially energy-independent. This approximation has often been used in calculating self-energy corrections in nonmetals. COHSEX only gives rather good quasi-particle energies near the gap, but the valence bandwidth comes out to be practically unrenormalized. In fact, from the calculated energy-dependence of the screened interaction it follows that COHSEX calculation is certainly reasonable in the vicinity of the band gap whereas dynamic screening effects have to be included for deep holes in the valence bands.

Finally we comment on the decay rate of quasi-holes in diamond. Fig. (3) shows the imaginary part of the quasi-particle levels with a hole in the valence bands along two symmetry directions. Since the mechanism responsible for the decay of the quasi-holes is the Coulomb interaction among the particles, we can call the radiationless transition to a final state with more than one hole in the valence bands an intraband Auger process. We notice from Fig. (3) that the decay rate vanishes (to within our numerical error) below a threshold, as expected. In addition, the rise in the decay for higher energies is in qualitative

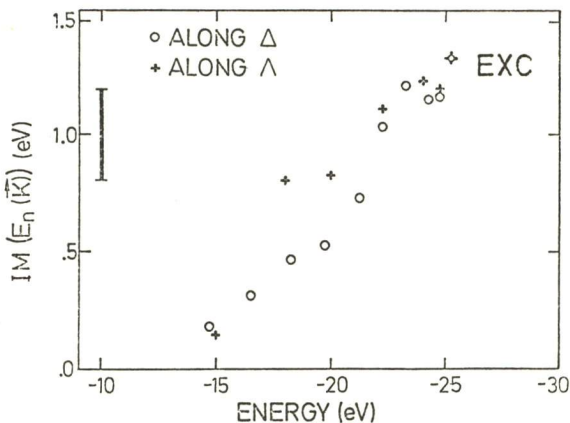


Fig.3: Quasi-particle decay (diamond)

agreement with empirical broadening factors that are necessary to relate XPS valence band spectra to the theoretical line-shape of the electronic density of states [10].

References

- 1) For a review see W. Hanke: Adv. in Phys. 27 (1978) 287.
- 2) Details of this work will be published by G. Strinati, H.J. Mattausch, and W. Hanke: to be submitted to Phys. Rev. B.
- 3) H.J. Mattausch, G. Strinati, and W. Hanke: to be submitted to Phys. Rev. B.
- 4) L.J. Sham and W. Kohn: Phys. Rev. 145 (1966) 561.
- 5) R.A. Roberts and W.C. Walker: Phys. Rev. 161 (1967) 730.
- 6) F.R. McFeely et al.: Phys. Rev. B 9 (1974) 5268.
- 7) A. Mauger and M. Lannoo: Phys. Rev. B 15 (1977) 2324.
- 8) A. Zunger and A.J. Freeman: Phys. Rev. B 15 (1977) 5049.
- 9) L. Hedin: Phys. Rev. 139 (1965) A796.
- 10) L. Ley, M. Cardona, and R.A. Pollak; in "Photoemission in Solids II", ed. by L. Ley and M. Cardona (Springer, Heidelberg, 1979), p.11.