

and uncompensated metals. To my knowledge, no other theory has been capable of predicting the observed diversity of behavior for the various coefficients of the two types of metals. Although I have been able to obtain reasonable quantitative agreement for some of the features of the present results, the fundamental parameter in the theory is f which is typically required to be $10^{-3} - 10^{-2}$, a range known to be too high.¹⁵ This suggests that the theory is still in need of modification and improvement.

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Dynamical Correlation Effects on the Quasiparticle Bloch States of a Covalent Crystal

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A local-orbital formulation of the Dyson equation is presented for the one-particle Green's function with the self-energy expressed in terms of a dynamically screened interaction which includes local-field and excitonic effects. Also presented is a quantitative calculation of the quasiparticle states for diamond from first principles, which demonstrates the different roles played by two-particle excitations (electron-hole, plasmon). A discussion of the implications for local-density and empirical one-electron concepts is given.

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The enormous success of energy-band calculations, using schemes such as the local-density approximation (LDA)¹ or the empirical (pseudo-) potential concept,² has given a kind of pragmatic answer of how to treat exchange and correlation effects on the one-electron states. On the other hand, the many-body theory of the solid state has established a number of more formal results, which may be viewed as a justification and first-principles basis for a one-electron theory.^{1,3-6} For metals, in particular for the idealized homogeneous electron-gas model, a large amount of convergence of the two directions has been

achieved.^{1,3-6} In semiconductors and insulators this is not so, basically because of the strong localization and inhomogeneity of the electronic states. Some of the difficulties are revealed by a comparison of recent LDA calculations^{7,8} with experimental gaps and valence-band widths, which show in both diamond (Table I) and silicon [$E_{\text{gap}}^{\text{LDA}} = 2.5$ eV vs $E_{\text{gap}}^{\text{exp}} = 3.4$ eV (Refs. 8, 9)] significant deviations. Empirical potentials, on the other hand, contain in a somewhat arbitrary manner higher-order [electron-hole (e-h), random-field approximation (RPA) local field] interaction effects.^{10,11}

TABLE I. Quasiparticle energies in diamond (in electron volts).

	E_{gap}	ΔE_{val}
E_{EXC}	7.4	25.2
E_{RPA}	8.25	26.1
E_{EH}	7.4	26.45
E_{SE}	7.2	28.83
LDA	6.3	20.4
HF	15.0	29.0
Expt.	7.3 - 7.6 ^a	24.2 ± 1 ^a

^aRef. 9.

This Letter reports results of investigations which aim at a first-principles understanding of one-electron quasiparticle states in covalent crystals. The self-energy or dynamical correlation potential is calculated with both its nonlocality in \vec{r} space and its energy dependence taken into account. It is obtained in the time-dependent screened Hartree-Fock (TDSHF) approximation by replacement of the exchange operator by a dynamically screened interaction.⁵ Previous calculations have used RPA frequency-independent or model dielectric functions,¹²⁻¹⁶ the electronic polaron,^{17,18} or the plasmon-pole approximation.¹⁹

We have investigated for the first time the role of a wave-vector and frequency-dependent dielectric function ϵ^{-1} which is calculated from first principles and includes RPA local-field and particle-hole (excitonic) effects. The correlated band structure is derived from a local-orbital representation of the equations of motion for one- and two-particle Green's functions,¹¹ exploiting, in particular, the short-range nature of the self-energy. It is shown for the prototype diamond (C) that the experimental band gap, the valence-band width, and the general features of quasiparticle decay observed in photoemission [x-ray photoemission spectroscopy (XPS)] data⁹ can be reproduced by such a first-principles calculation. Interrelations with the "screened exchange plus Coulomb hole" (SECH) approximation⁵ and the LDA are pointed out. For example, we find the quasiparticle energy near the gap basically determined by the coupling to e-h pairs, thereby suggesting a local (LDA) quasiparticle description³ to be appropriate in this energy range.

Our starting point is the Schrödingerlike equation for the quasiparticle states^{3,5} with wave functions $\Psi_{n\vec{k}}(\vec{r})$. Expanding the $\Psi_{n\vec{k}}(\vec{r})$ in a set of orbitals $\varphi_\gamma(\vec{r} - \vec{I})$ that are localized about the N lattice sites \vec{I} , we arrive at an eigenvalue equation for the expansion coefficients $c_{\gamma n}(\vec{k})$:

$$\sum_{\gamma'} \{ \sum_{\vec{I}} e^{i\vec{k} \cdot \vec{I}} [\langle \varphi_{\gamma'}(\vec{r}) | h(\vec{r}) | \varphi_{\gamma'}(\vec{r} - \vec{I}) \rangle + \langle \varphi_{\gamma'}(\vec{r}) | \Sigma(\vec{r}, \vec{r}'; E) | \varphi_{\gamma'}(\vec{r} - \vec{I}) \rangle] \} c_{\gamma' n}(\vec{k}) = \xi_{n\vec{k}}(E) c_{\gamma n}(\vec{k}), \quad (1)$$

with the condition $E - \xi_{n\vec{k}}(E) = 0$ determining the quasiparticle energies $E_{n\vec{k}}$. In general $E_{n\vec{k}}$ is complex, with its real part furnishing a physical energy and its imaginary part the decay rate. Because of both the short-range properties of Σ (Ref. 3) and the localization of the orbitals φ_γ , one expects the \vec{I} summation over the matrix elements of the self-energy Σ to be similarly restricted to a few shells of neighbors as in the matrix elements of the Hartree term h in Eq. (1). We employ the TDSHF approximation for the self-energy which consists in replacing the static bare Coulomb interaction in the HF operator by a dynamically screened interaction $W = v\epsilon^{-1}$.⁵

Expressing the one-particle Green's function g in local-orbital representation,

$$g(\vec{r}, \vec{r}'; E) = \sum_{\vec{\sigma}} \sum_{\vec{\sigma}'} \varphi_{\vec{\sigma}}(\vec{r} - \vec{\sigma}) g_{\vec{\sigma}\vec{\sigma}'}(\vec{\sigma} - \vec{\sigma}'; E) \varphi_{\vec{\sigma}'}^*(\vec{r}' - \vec{\sigma}'), \quad (2)$$

where

$$g_{\vec{\sigma}\vec{\sigma}'}(\vec{\sigma} - \vec{\sigma}'; E) = \sum_n N^{-1} \sum_{\vec{k}} \frac{c_{\vec{\sigma}n}^{(0)}(\vec{k}) \exp[i\vec{k} \cdot (\vec{\sigma} - \vec{\sigma}')] c_{\vec{\sigma}'n}^{(0)*}(\vec{k})}{E - E_{n\vec{k}}^{(0)} + i\delta \operatorname{sgn}(E_{n\vec{k}}^{(0)} - E_F)}, \quad (3)$$

we get for the matrix elements of the mass operator Σ' (only the non-HF part) after some rearrangements

$$\begin{aligned} & \langle \varphi_\gamma(\vec{r}) | \Sigma'(\vec{r}, \vec{r}'; E) | \varphi_{\gamma'}(\vec{r}' - \vec{I}) \rangle \\ &= \frac{i}{2\pi N} \int_0^\infty dE' \sum_{\vec{\sigma}\vec{\sigma}'} \sum_{\vec{m}\vec{m}'} \{ g_{\vec{\sigma}\vec{\sigma}'}(-\vec{m}; E + E') + g_{\vec{\sigma}\vec{\sigma}'}(-\vec{m}; E - E') \} \sum_{\vec{q}}^{\text{BZ}} e^{-i\vec{q} \cdot \vec{m}} W'_{\vec{m}+\vec{m}'; \vec{\sigma}\vec{\sigma}'}(\vec{q}, E'), \end{aligned} \quad (4)$$

with (in matrix notation)

$$W'(\vec{q}, E) = V(\vec{q})G(\vec{q}, E)V(\vec{q}). \quad (5)$$

Here V denotes the Coulomb matrix and G the screening matrix or two-particle Green's function in local-orbital representation.¹¹

To be consistent with a variety of experimental facts the two-particle Green's function is also treated within TDSHF. This amounts to inclusion of RPA local-field and e-h attraction effects (exchange-correlation beyond RPA). Hanke and Sham have shown that these corrections are essential for a quantitative understanding of the optical spectra of insulators¹⁰ and semiconductors,¹¹ and we recently have found them also to be indispensable in calculating the screening of impurities.²⁰ With the help of the local-orbital representation the Bethe-Salpeter equation for the two-particle Green's function can be cast in a matrix equation¹¹ and inverted, with G given by

$$G = G^0[1 - (V - V_{\text{exc}})G^0]^{-1}, \quad (6)$$

where G^0 is the noninteracting e-h pair. If the e-h attraction $-V_{\text{exc}}$ is omitted, the result in Eq. (6) with just the unscreened Coulomb repulsion V reduces to the usual RPA.

$c^{(0)}$ and $E^{(0)}$ in Eq. (3) denote a zeroth-order approximation for the quasiparticle states which in our calculation for diamond is extracted from an $X\alpha$ band calculation.²¹ This band structure is fitted in terms of a fourth-nearest-neighbor overlap model of bonding and antibonding orbitals as described in the earlier work on the optical response of C.¹⁰ Also the calculation of the two-particle Green's function is based on this band structure and follows closely the optical work (details can be found in Ref. 10)—however, now with ω and \vec{q} dependence included. The orbitals φ_γ , determining the one-particle Green's function g in Eq. (2), the screened interaction W , and finally the self-energy matrix elements in Eq. (4), are adjusted as in Ref. 10 such that current conservation is fulfilled. The justification for this "short cut" in the self-consistency circle for the $E_{n\vec{k}}$ and $\Psi_{n\vec{k}}$ is only a pragmatic one, in that in this case the two-particle excitations are found in quantitative agreement with a variety of experimental data.^{10,20} Also the sum rules for ϵ and ϵ^{-1} are fulfilled to within 10% of the exact values. The HF part of the matrix elements in the quasiparticle equation (1) is taken from a similar fourth-nearest-neighbor fit to the self-consistent HF energy bands of a recent HF cal-

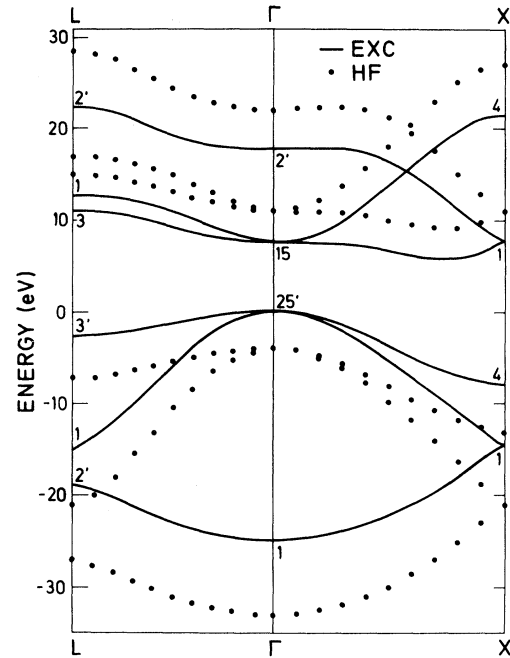


FIG. 1. Quasiparticle band structure of diamond. HF denotes self-consistent HF results from Ref. 22. EXC gives results in TDSHF, with the dynamical screening including RPA (local-field) and particle-hole (excitonic) effects.

ulation by Mauger and Lannoo.²² With self-energy matrix elements added, Eq. (1) is then diagonalized in the local-orbital basis with the equation $\xi_{n\vec{k}}(E) - E = 0$ solved numerically for the quasiparticle energies $E_{n\vec{k}}$.

Results for the quasiparticle band structure of C are plotted in Fig. 1 on an absolute energy scale for two \vec{k} directions. The points denote self-consistent HF energy bands,²² which give a gap of about 15 eV compared to 7.3–7.6 in reflectivity experiments, and a valence-band width of 29 eV, compared to 24.2 ± 1 eV in XPS data.⁹ The full lines (EXC) present our final results for the quasiparticle spectrum, where the two-particle Green's function G contains both RPA (including local-field) and e-h attraction effects. The gap is drastically reduced from the HF value to 7.4 eV and also the valence-band width to 25.2 eV, in quantitative agreement with the experimental values. If we resort just to the RPA and leave out the e-h attraction [$V_{\text{exc}} = 0$ in Eq. (6)] in the screened interaction W , both the gap and the bandwidth increase by about 1 eV compared to the full calculation (E_{RPA} in Table I). This point shows the necessity of an accurate description of

two-particle excitations,^{10,11} which in turn renormalize the one-electron-like excitations. The third column in Table I gives the gap and bandwidth of a calculation where the plasmon contribution (in C at about 35 eV) is chopped off by restricting the energy integration in Eq. (4) to 32 eV. The gap is found unchanged (7.4 eV) and, therefore, the quasiparticle properties in the vicinity of the gap are essentially entirely determined by coupling to e-h excitations. Since the e-h correlation effect is predominantly short ranged, this leads to a justification of a "local" correlation concept in this energy range, possibly along the lines of the quasiparticle LDA concept.^{3,23}

The valence-band width is found in this calculation with the plasmon cutoff as 26.45 eV, and, thus, predominantly nonlocal plasmon-type correlations introduce a shrinking of about 1.25 eV. However, also for the bandwidth, the dominating self-energy correction stems from e-h excitations which renormalize the HF value (29 eV) down to 26.45 eV.

We have tested the often-used¹²⁻¹⁵ SECH approximation⁵ which essentially amounts to the assumption that W is independent of frequency ($\omega = 0$). SE only gives rather good quasiparticle energies near the gap ($E_{\text{gap}}^{\text{SE}} = 7.2$ eV) but the valence-band width comes out to be more or less unrenormalized (28.83 eV). From the ω dependence of the screened interaction W , which is essentially constant up to 10 eV, it follows that the combined SE+CH calculation is certainly reasonable to about 10 eV away from the gap in C; from there on (note that W is weighted with a strongly peaked function g) dynamic screening effects have to be

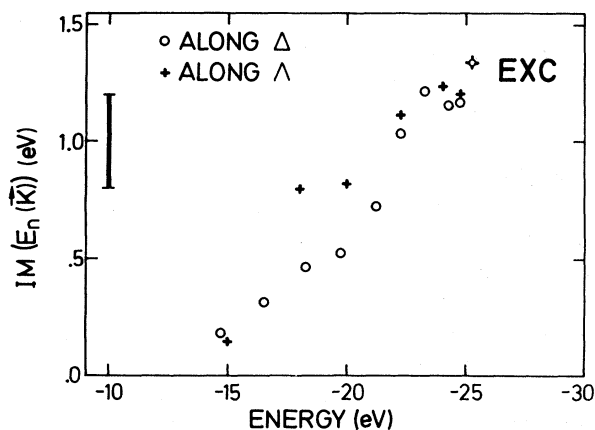


FIG. 2. Quasiparticle decay (valence bands) in diamond as function of energy.

included which becomes obvious near the plasmon pole.

Finally, let us briefly comment on the decay rate of the quasiparticles shown in Fig. 2 for two symmetry directions in C. $\text{Im}E_{n\mathbf{k}} = 0$ below a threshold which amounts to the minimum energy to create e-h pairs. The second general feature is the expected rise in the decay for higher energies, in qualitative accordance with empirical broadening factors which are necessary to relate XPS valence-band spectra to theoretical line shapes of the electron density of states.⁹

Summarizing, on the basis of an accurate description of the two-particle Green's function,^{10,11} which is consistent with a variety of experimental facts, an investigation has been performed on the quasiparticle properties, in particular on the dynamical correlation potential in strongly inhomogeneous crystals. It has been shown for the prototype diamond that the experimental data on the single-particle-like spectrum can be reproduced from first-principles work. New insights for the applicability and also the limitations of much-used one-electron schemes have emerged.

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NMR Measurement of the Hyperfine Constant of an Excited State of an Impurity Ion in a Solid

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An optically detected NMR measurement of the hyperfine tensor for an excited state of an impurity rare-earth ion (Pr^{3+}) in a solid (LiYF_4) is reported. The results have been used to obtain for the first time a measured value of the hyperfine interaction constant $A_j = 616 \pm 51$ MHz of the 1D_2 excited state. This is somewhat smaller than the calculated value of 754 MHz.

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We report the first excited-state nuclear magnetic resonance (NMR) observation. From a measurement of the orientation and magnitude of the nuclear Zeeman tensor of the diamagnetic 1D_2 ($16\,740\text{ cm}^{-1}$) level of trivalent praseodymium dilute in the LiYF_4 single crystal, we have obtained the magnetic hyperfine constant¹ A_j for this $^1D_2(4f^2)$ state. Earlier excited-state magnetic-resonance observations were studies of paramagnetic levels.²⁻⁶

The large nuclear polarization (and population) required for the NMR observation is obtained by high-resolution optical pumping within a strain-broadened inhomogeneous optical line which selects individual hyperfine states. Using this polarization scheme, Erickson⁷ has studied the ground-state hyperfine interaction in the trivalent praseodymium in LaF_3 and YAlO_3 host crystals. We have extended his optical rf double-resonance technique to an excited state of trivalent praseodymium.

Excited-state studies by Chen, Chiang, and Hartmann⁸ have determined the hyperfine splitting of the 3P_0 state of Pr^{3+} in LaF_3 from their modulated photon-echo experiments. Erickson,^{9,10} using an enhanced and saturated optical-absorption

technique, has measured the hyperfine splittings of the lowest level of the 1D_2 manifold of states of Pr^{3+} in LaF_3 and YAlO_3 . The hyperfine constant A_j was not obtained in those studies. Although in principle it should be possible to determine A_j from the hyperfine splittings alone, the lack of the precise knowledge of the pure quadrupole coupling constants and the electronic wave functions make this determination difficult at best. A_j can, however, be determined from knowledge of the nuclear Zeeman tensor without knowing the pure quadrupole constants. The $\text{LiYF}_4:\text{Pr}^{3+}$ system was chosen for study because (i) the $(4f^2)$ electron configuration is the simplest nontrivial rare-earth configuration, (ii) the lowest states of 1D_2 and 3H_4 are singlets, and (iii) best-fit crystal-field wave functions are available.¹¹ The low-magnetic-field study of the Pr^{3+} ion in this single-magnetic-site host is greatly simplified compared to the three-magnetic-site LaF_3 host. This magnetic site is axially symmetric, further reducing the complexity (and uncertainty) of the analysis.

We believe a variation of this excited-state NMR technique can be used to obtain the hyperfine and nuclear Zeeman tensors of other systems with nondegenerate electronic states which are in-