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Correlated Hartree-Fock energy bands for diamond

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The screened-exchange–plus–Coulomb-hole method has been used to add correlation to Hartree-Fock energy bands. These correlation corrections, or energy shifts, are state dependent due to the screened-exchange term. The Coulomb-hole term is constant throughout the zone in our diagonal approximation for the screening (dielectric) function. The energy shifts raise the occupied bands and lower the conduction bands with a resulting decrease in energy differences. The calculation has been done for diamond using linear combination of atomic orbitals Hartree-Fock bands and the Penn-model dielectric function. The energy shifts, which tend to flatten the bands, were computed at general points in the first zone. Values of 5.6 and 7.6 eV were obtained for the indirect and direct band gaps respectively, both of which are in close agreement with experiment. The diagonal part of the random-phase approximation was also used in the calculation and it was found to produce about two-thirds of the correlation obtained with the Penn model.

I. INTRODUCTION

Since diamond is a relatively simple example of a covalently bonded crystal, there has been a great deal of interest in it which has led to many energy-band calculations. Recent band calculations have been done by Herman *et al.*[1] using the orthogonalized-plane-wave (OPW) method, Saslow *et al.*[2] using the empirical pseudopotential method, Chaney *et al.*[3] using the tight-binding method, Keown[4] using the augmented-plane-wave (APW) method, and Bassani and Yoshimine[5] using the OPW method. Of these calculations, only Herman's is self-consistent, but since his self-consistent band gaps are too small, he adds an empirical correction in order to match the experimental indirect gap. The calculations of Saslow *et al.* and Keown are also empirically adjusted to match experiment. The calculations of Chaney *et al.* and Bassani *et al.* use the Slater approximation for the exchange potential which yields energy differences that are too small in comparison with experiment. In this paper, exact, self-consistent Hartree-Fock energy bands rather than $X\alpha$ bands are used and correlation corrections are included by using many-body theory rather than by making empirical adjustments to experimental band gaps.

The Hartree-Fock energy bands used in this paper were computed by Euwema *et al.*[6] using the linear-combination-of-atomic-orbitals (LCAO) method. Gaussian lobes were used for the atomic S and P orbitals, which made up a basis set consisting of contracted $1s$, $2s$, and $2p$ orbitals and individual $3s$, $4s$, $3p$, and $4p$ orbitals. All of the integrals involved in the Hamiltonian matrix elements were computed in direct space, eliminating the problem of slowly convergent reciprocal lattice sums. The direct lattice sums were carried out to four or five place accuracy with the aid of three charge-conserving integral approximations.[7] The Hartree-Fock bands were used to compute electron Compton profiles,[8] the equilibrium lattice constant, and the bulk modulus,[9] all of which were in close agreement with experiment. An equilibrium lattice constant of 3.545 Å and bulk modulus of 4.38×10^{12} dyn/cm^2 were obtained, and were compared with experimental values of 3.567 Å and 4.42×10^{12} dyn/cm^2, respectively.

As is well known, Hartree-Fock band calculations give energy differences that are too large so that correlation corrections must be added to the bands in order to obtain more favorable agreement with experiment. Various methods have been developed for adding correlation to Hartree-Fock energies including the electronic polaron method of Kunz[10] and the random-phase approximation (RPA) approach of Monkhorst *et al.*[11] In our calculation we use the screened-exchange–plus–Coulomb-hole (SECH) method which was first proposed by Hedin[12] in 1965 and later treated in more detail by Hedin and Lundqvist.[13] Previous crystalline calculations employing this method have been done by Brinkman and Goodman[14] using $X\alpha$ rather than Hartree-Fock energy bands and by Lipari and Fowler[15] who used non-self-consistent approximate Hartree-Fock bands. In both of these calculations the Penn-model dielectric function was used and the energies were computed only at symmetry points. In this paper, true self-consistent Hartree-Fock energy bands are used, the energies are computed at general points in the Brillouin zone, and the calculation is done with the RPA dielectric function, the one that actually appears in the SECH method, as well as with the Penn model.

II. SUMMARY OF FORMALISM

Following Hedin and Lundqvist,[13] one can use Green's function techniques to derive an expression for the SECH correlation corrections. As the author has treated this derivation in detail in another paper,[16] it will merely be summarized here. In a single particle theory the one-electron states u_k and corresponding energies ϵ_k satisfy the equation

$$[h(\vec{r}_1)+V(\vec{r}_1)]\,u_k(\vec{r}_1)+\int \Sigma(\vec{r}_1,\vec{r}_2)u_k(\vec{r}_2)\,d\vec{r}_2=\epsilon_k u_k(\vec{r}_1), \tag{1}$$

where h is the kinetic energy plus the interaction of the electron with the nuclei, V is the Coulomb repulsion due to the other electrons, and Σ is the self-energy which contains all the exchange and correlation effects. Equation (1) applies whenever the self-energy is independent of frequency, which is generally not the case. In the SECH method, we expand the self-energy in powers of a dynamically screened interaction $W(\vec{r}_1, \vec{r}_2, t_1-t_2)$, rather than a bare instantaneous Coulomb interaction, and keep the first term. Since the screened interaction is a sharply peaked function of t_1-t_2, we replace it by its integrated value times a delta function, which corresponds to an averaged instantaneous interaction. When the Fourier transform with respect to t_1-t_2 is then taken, we obtain the frequency-independent SECH approximation for the self-energy

$$\begin{aligned}\Sigma_{\text{SECH}}(\vec{r}_1,\vec{r}_2)=&-\rho(\vec{r}_1,\vec{r}_2)\,W(\vec{r}_1,\vec{r}_2,\omega=0)\\&+\tfrac{1}{2}\,\delta(\vec{r}_1,\vec{r}_2)[W(\vec{r}_1,\vec{r}_2,\omega=0)-v(\vec{r}_1,\vec{r}_2)],\end{aligned} \tag{2}$$

$$\rho(\vec{r}_1,\vec{r}_2)=\sum_{k\ \text{occ.}} u_k^*(\vec{r}_2)\,u_k(\vec{r}_1),$$

$$v(\vec{r}_1,\vec{r}_2)=e^2/|\vec{r}_1-\vec{r}_2|,$$

where ω is the frequency, e is the charge of an electron, and the screened interaction W is defined in terms of the dielectric response function ϵ,

$$W(\vec{r}_1,\vec{r}_2,\omega)=\int v(\vec{r}_1,\vec{r}_3)\epsilon^{-1}(\vec{r}_3,\vec{r}_2,\omega)\,d\vec{r}_3\,. \tag{3}$$

The first term in Eq. (2) leads to a statically screened exchange (SE) while the second produces a Coulomb hole (CH).

If the self-energy were given by

$$\Sigma_{\text{HF}}(\vec{r}_1,\vec{r}_2)=-\rho(\vec{r}_1,\vec{r}_2)v(\vec{r}_1,\vec{r}_2),$$

then Eq. (1) would become the Hartree-Fock (HF) equation which has only an unscreened exchange term. Let us denote the HF one-electron wave functions and energies by $u_{\vec{k}n}$ and $\epsilon_{\vec{k}n}$, respectively, where $\vec{k}$ is a reciprocal space vector restricted to the first zone and n is a band index. Since we are already in possession of a set of HF wave functions and energies, we can use first-order perturbation theory to obtain corrections $\Delta\epsilon_{\vec{k}n}$ to the HF energies due to using Σ_{SECH} in Eq. (1). Considering the HF Hamiltonian to be unperturbed and letting the difference between Σ_{SECH} and Σ_{HF} be the perturbation, the correction to the energy is then given by

$$\begin{aligned}\Delta\epsilon_{\vec{k}n}=&-\int u_{\vec{k}n}^*(\vec{r}_1)\rho(\vec{r}_1,\vec{r}_2)\\&\times[W(\vec{r}_1,\vec{r}_2,\omega=0)-v(\vec{r}_1,\vec{r}_2)]\,u_{\vec{k}n}(\vec{r}_2)\,d\vec{r}_1\,d\vec{r}_2\\&+\frac{1}{2}\int u_{\vec{k}n}^*(\vec{r}_1)\delta(\vec{r}_1,\vec{r}_2)\\&\times[W(\vec{r}_1,\vec{r}_2,\omega=0)-v(\vec{r}_1,\vec{r}_2)]\,u_{\vec{k}n}(\vec{r}_2)\,d\vec{r}_1\,d\vec{r}_2\,.\end{aligned} \tag{4}$$

These energy shifts, which are correlation corrections, have been obtained by using Green's-function theory to go beyond the HF approximation.

Expressing the bare and screened interactions in terms of their Fourier transforms, we have

$$v(\vec{r}_1,\vec{r}_2)=\frac{1}{(2\pi)^3}\int v(\vec{q})e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)}\,d\vec{q}\,, \tag{5}$$

$$W(\vec{r}_1,\vec{r}_2,\omega)=\frac{1}{(2\pi)^6}\int W(\vec{q},\vec{q}\,',\omega)e^{i\vec{q}\cdot\vec{r}_1-i\vec{q}\,'\cdot\vec{r}_2}\,d\vec{q}\,d\vec{q}\,', \tag{6}$$

$$W(\vec{q},\vec{q}\,',\omega)=v(\vec{q})\epsilon^{-1}(\vec{q},\vec{q}\,',\omega), \tag{7}$$

$$v(\vec{q})=4\pi e^2/q^2\,. \tag{8}$$

The HF states, which are calculated using the LCAO method, have the form

$$u_{\vec{k}n}(\vec{r})=\frac{1}{\sqrt{N}}\sum_{i\nu} b_{ni}(\vec{k})e^{i\vec{k}\cdot\vec{R}_\nu}\phi_i(\vec{r}-\vec{R}_\nu), \tag{9}$$

where the sums are over atomic orbitals ϕ_i and direct lattice vectors $\vec{R}_\nu$, the b_{ni}'s are the coefficients of the Bloch functions associated with the atomic orbitals and N is the number of unit cells in the crystal. Using (9), the Fourier transform of the dielectric function can be written

$$\begin{aligned}\epsilon(\vec{q},\vec{q}\,',\omega)=&(2\pi)^3\delta(\vec{q}\,'-\vec{q})\\&-\sum_{\vec{K}_2} P(\vec{q},\vec{q}+\vec{K}_2,\omega)v(\vec{q}+\vec{K}_2)\delta(\vec{q}\,'-\vec{q}-\vec{K}_2),\end{aligned} \tag{10}$$

where P is the polarization and $\vec{K}_2$ is a reciprocal-lattice vector.

We now make the approximation of keeping only the $\vec{K}_2 = 0$ term in (10), in which case the inverse dielectric function is readily obtained

$$\epsilon^{-1}(\vec{q}, \vec{q}\,', \omega) = [(2\pi)^3/\epsilon(\vec{q}, \omega)]\, \delta(\vec{q}, \vec{q}\,'), \tag{11}$$

$$\epsilon(\vec{q}, \omega) = 1 - [1/(2\pi)^3]\, v(\vec{q}) P(\vec{q}, \vec{q}, \omega), \tag{12}$$

$$P(\vec{q}, \vec{q}, \omega) = \frac{2(2\pi)^3}{V_c} \sum_{\vec{k} n n'} \frac{\eta_{\vec{k}+\vec{q}+\vec{K}_1, n} - \eta_{\vec{k} n'}}{\epsilon_{\vec{k}+\vec{q}+\vec{K}_1, n} - \epsilon_{\vec{k} n'} - \omega} \times \left| \langle \vec{k} n' \,|\, e^{-i\vec{q}\cdot\vec{r}} \,|\, \vec{k}+\vec{q}+\vec{K}_1, n \rangle \right|^2 . \tag{13}$$

The factor of 2 in front of the sum is due to spin, V_c is the volume of the crystal, $\eta_{\vec{k}n}$ is the occupation number (either 0 or 1) of the state $u_{\vec{k}n}$, $\vec{K}_1$ is the reciprocal-lattice vector such that $\vec{k} + \vec{q} + \vec{K}_1$ is in the first zone, and $|\vec{k}n\rangle = u_{\vec{k}n}$.

Using Eqs. (5)–(9) and (11), the energy shifts can be written

$$\Delta\epsilon_{\vec{k}n} = -\frac{1}{V_c} \sum_{\vec{K}, \vec{k}', n' \,\mathrm{occ.}} \left| \langle \vec{k}' n' | e^{-i(\vec{k}-\vec{k}'+\vec{K})\cdot\vec{r}} |\vec{k}n\rangle \right|^2 v(\vec{k}-\vec{k}'+\vec{K}) \times \left(\frac{1}{\epsilon(\vec{k}-\vec{k}'+\vec{K}, \omega=0)} - 1 \right) + \frac{1}{2(2\pi)^3} \int v(\vec{q}) \left(\frac{1}{\epsilon(\vec{q}, \omega=0)} - 1 \right) d\vec{q}, \tag{14}$$

where the sum on $\vec{K}$ is over reciprocal lattice vectors. These energy shifts are state dependent due to the $|\vec{k}n\rangle$ dependence in the first term, which is the difference between a screened and unscreened exchange. The second term, the Coulomb hole, is constant in our diagonal approximation for the dielectric function; however, if the full dielectric matrix rather than just the diagonal part is used, then the Coulomb-hole term is also state dependent. Making the approximation that the dielectric function $\epsilon(\vec{q}, \omega = 0)$ falls off to 1 outside of the first zone, we keep only the reciprocal-lattice vector $\vec{K}$ in the above sum such that $\vec{k} - \vec{k}' + \vec{K}$ is in the first zone, and we limit the $\vec{q}$ integration in (14) to the first zone. Since the factor $1/\epsilon - 1$ appears in both terms of (14), the above approximation neglects positive and negative terms which, in addition to being small, cancel each other to some extent.

III. RESULTS FOR DIAMOND

The dielectric function used in this calculation is the diagonal part of the one appearing in Eq. (10), which is called the RPA dielectric function. Since we are using first-order perturbation theory to obtain the energy shifts, the dielectric function must be computed with HF wave functions and energies. The HF eigenvectors and energies were initially determined at 20 points in $\frac{1}{48}$th of the Brillouin zone, and then the eigenvectors [the coefficients b_{ni} in Eq. (9)] were permuted to obtain the HF wave functions at 341 points throughout the zone. These 341 zone points were used to compute the diagonal part of the RPA at 20 points in $\frac{1}{48}$th of the first zone, with the 6 occupied bands and lowest 12 conduction bands being included in the computation. As shown by Table I, the RPA appears to be well converged after 12 conduction bands.

A simpler expression for the dielectric function is provided by the Penn model[17] which is a semiempirical model that takes on the experimental value for the optical dielectric constant when $\vec{q} = 0$. Figure 1 compares the RPA computed with HF wave functions and energies (HF RPA), the RPA computed with HF wave functions and SECH correlated energies (SECH RPA), and the Penn-model dielectric function. We see that the HF RPA is smaller than the experimental value as represented by the Penn model, with the difference being due partly to the uncorrelated energy differences that appear in the denominator of Eq. (13). The SECH RPA curve shows that correcting

TABLE I. RPA for diamond at $\vec{q} = (\pi/2a)$ (1, 0, 0) vs total number of conduction bands used in calculation.

Bands	$\epsilon(\vec{q}, 0)$
1	1.885
2	2.348
3	2.668
4	2.760
5	2.776
6	2.791
7	2.803
8	2.812
9	2.817
10	2.820
11	2.821
12	2.822

these HF energy differences makes up less than half of the difference between the HF RPA and the Penn model. Three factors which contribute to the remaining difference between the HF RPA and experiment are the uncorrelated wave functions appearing in the matrix elements in Eq. (13), the neglect of higher-order polarization terms beyond the RPA, and the neglect of the off-diagonal terms of the dielectric matrix [the $\vec{K}_2 \neq 0$ terms in Eq. (10)] which correspond to local field effects. Since we have computed only the diagonal part of the RPA thus far, the Penn model will be used to calculate the SECH energy shifts; however, a comparison will be made with the energy shifts obtained using the HF RPA and the SECH RPA.

The author has done the calculation described above for LiF,[16] in which case greater differences were found between the HF RPA and the Penn model than in the case of diamond. Also the SECH RPA made up a considerably smaller part of this difference in LiF than in the case of diamond, indicating that the three factors mentioned above may be more important in LiF than in diamond.

Figure 2 shows the uncorrelated HF energy bands which yield energy differences that are too large in comparison with experiment. The corresponding HF eigenvectors were determined at 341 points throughout the Brillouin zone and then used to compute the SECH energy shifts for the 6 occupied bands and first 12 conduction bands at 20 points in $\frac{1}{48}$th of the first zone. For core and valence bands, the first term in Eq. (14) is larger than the second, producing positive energy shifts, while for conduction bands, the Coulomb-hole term dominates and the energy shifts are negative. Thus, the correlation corrections raise the occupied bands and lower the conduction bands with a resulting decrease in energy differences. Energy shifts, obtained with the Penn model dielectric function, are shown in Table II for several points in the first zone. These shifts are quite state dependent, varying by as much as 2 eV over the zone and by as much as 3 eV (in magnitude) over bands. In general, the correlation corrections tend to flatten the bands, e.g., the shifts for the Δ_5 and Δ_2' valence bands increase while the shift for the Δ_1 valence band decreases as one moves out from the center of the zone along the Δ axis.

Table III gives a comparison of SECH band-gap changes ΔE_g obtained with the HF RPA, the SECH

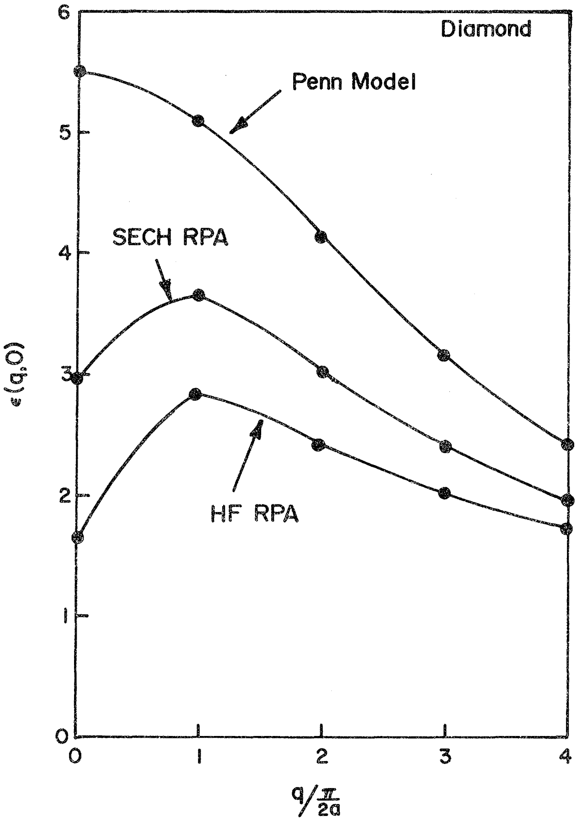

FIG. 1. Diamond dielectric functions along the Δ axis.

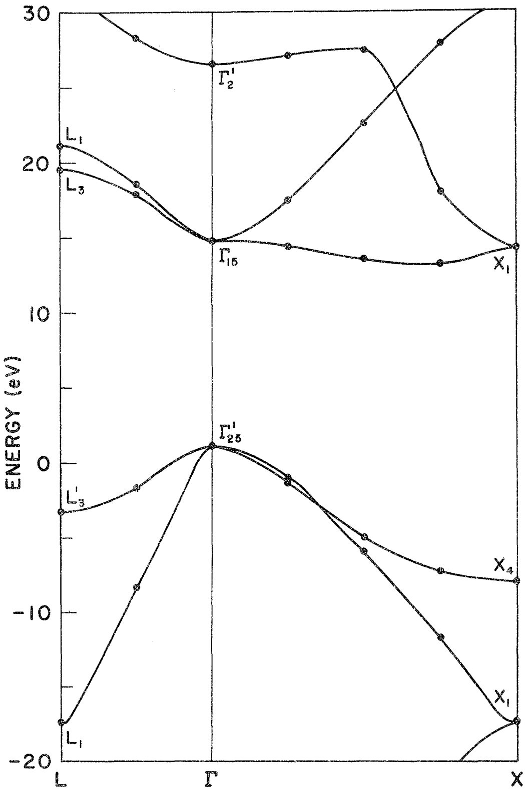

FIG. 2. Uncorrelated HF energy bands for diamond.

TABLE II. SECH energy shifts for diamond at several points $\vec{q}$ in the first Brillouin zone. Shifts are in eV.

$\vec{q}$	Valence			Conduction		
	Γ_1	Γ'_{25}	Γ'_{25}	Γ_{15}	Γ_{15}	Γ'_2
$(\pi/2a)(0,0,0)$	5.53	2.45	2.45	−3.61	−3.61	−4.95
	Δ_1	Δ'_2	Δ_5	Δ_1	Δ_5	Δ'_2
(1,0,0)	5.52	2.66	2.57	−3.69	−3.81	−4.96
(2,0,0)	5.45	3.32	3.10	−3.84	−4.44	−4.98
(3,0,0)	5.23	4.09	3.51	−4.01	−4.98	−4.55
	X_1	X_1	X_4	X_1	X_3	X_1
(4,0,0)	4.77	4.77	3.68	−4.24	−5.23	−4.24
	Λ_1	Λ_1	Λ_3	Λ_3	Λ_1	Λ_1
(1,1,1)	5.48	3.37	2.78	−4.00	−4.14	−5.03
	L'_2	L_1	L'_3	L_3	L_1	L'_2
(2,2,2)	5.09	4.72	3.14	−4.29	−4.51	−5.33

RPA, and the Penn model dielectric functions. We see that the diagonal parts of the HF RPA and SECH RPA produce, respectively, about $\frac{2}{3}$ and $\frac{5}{6}$ of the correlation obtained with the Penn model. Thus the correlated energies used in the SECH RPA make up about half of the difference between the HF RPA and Penn-model results. The SECH RPA gap changes are relatively close to the Penn-model results but still differ from them by an eV or more.

Figure 3 shows the SECH correlated energy bands while Table IV compares the corresponding SECH correlated energy differences, obtained with the Penn model, to the uncorrelated HF energy gaps at a few symmetry points. We see that the SECH correlation corrections significantly reduce the HF gaps, producing changes of almost 9 eV in some cases. The table also makes comparisons with experimental values for some of the energy differences and we see that the SECH results are in close agreement with the experimental indirect and direct band gaps. The agreement is best for the indirect gap which is the only piece of "hard" experimental information available for diamond. Thus the SECH method provides most of the correlation needed in diamond for the top of the valence band.

TABLE III. Comparison of diamond band-gap changes ΔE_g obtained with the HF RPA, SECH RPA, and Penn-model dielectric functions. Gap changes are in eV.

	$\Delta E_g^{\text{HF RPA}}$	$\Delta E_g^{\text{SECH RPA}}$	$\Delta E_g^{(\text{Penn})}$
$\Gamma'_{25}\rightarrow\Delta_1$	4.3	5.5	6.5
$\Gamma'_{25}\rightarrow\Gamma_{15}$	4.0	5.1	6.1
$X_4\rightarrow X_1$	5.4	6.7	7.9
$X_4\rightarrow X_3$	6.1	7.6	8.9
$L'_3\rightarrow L_3$	5.0	6.3	7.4

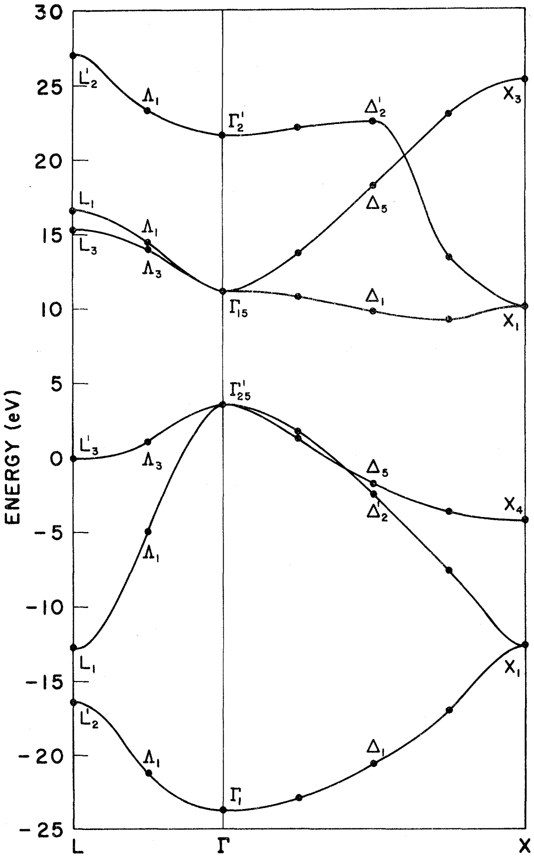

FIG. 3. SECH correlated energy bands for diamond.

TABLE IV. Diamond HF and SECH energy differences in eV. Some experimental values are also given.

	HF	SECH	Experiment
$\Gamma'_{25}\rightarrow\Delta_1$	12.1	5.6	5.5– 5.6 [a]
$\Gamma'_{25}\rightarrow\Gamma_{15}$	13.7	7.6	7.3– 7.4 [b]
$\Gamma_1\rightarrow\Gamma'_{25}$	30.3	27.2	24.2 [c]
$\Gamma'_{25}\rightarrow\Gamma'_2$	25.5	18.1	
$X_4\rightarrow X_1$	22.2	14.3	12.5–12.6 [b]
$X_4\rightarrow X_3$	38.5	29.6	
$L'_3\rightarrow L_3$	22.8	15.3	
$L'_3\rightarrow L_1$	24.3	16.7	
$L'_3\rightarrow L'_2$	35.6	27.2	

[a] References 18–20.

[b] Reference 19 and 20.

[c] Reference 21.

The Penn-model dielectric function is derived as an approximation to the diagonal part of the RPA; however, it is then forced to assume the experimental value for the optical dielectric constant when $\vec{q}=0$. The fact that the Penn model gives such good correlated energy differences indicates that if one uses a dielectric function having the proper (experimental) $\vec{q}=0$ behavior, then the SECH method works well in the case of diamond.

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