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Screened-exchange plus Coulomb-hole correlated Hartree-Fock energy bands for LiF

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Green's-function techniques have been used to derive screened-exchange plus Coulomb-hole correlation corrections to Hartree-Fock energy bands. These correlation corrections or energy shifts consist of a statically screened exchange term which is state dependent, and a Coulomb-hole term which is constant in our diagonal approximation for the screening (dielectric) function. These energy shifts raise the occupied bands and lower the conduction bands with a resulting decrease in energy differences. The calculation was done for LiF at general points in the first zone using linear-combination-of-atomic-orbitals Hartree-Fock energy bands and the Penn-model dielectric function. A change in.the band gap at Γ of 5.0 eV was obtained compared with the experimental value of 9.3 eV. The calculation was also done using the random-phase-approximation (RPA) dielectric function and it was found that the diagonal part of the RPA gives less than half of the correlation obtained with the Penn model.

I. INTRODUCTION

In the past few years, several methods have been developed for calculating true Hartree-Fock energy bands rather than $X\alpha$ bands in which the exchange term is approximated by $\rho^{1/3}$. Crystalline Hartree-Fock calculations have been done by Euwema and coworkers[1-3] using the linear-combination-of-atomic-orbitals (LCAO) method, by Mickish *et al.*[4] using a localized-orbital method, and by Kumar *et al.*[5] using Fourier-transform techniques. 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[6] and the random-phase-approximation (RPA) approach of Monkhorst and Oddershede.[7] In this paper we use the screened-exchange–plus–Coulomb-hole (SECH) method for adding correlation to Hartree-Fock energy bands.

The SECH method was first proposed by Hedin[8] in 1965 and later treated in more detail in a review article by Hedin and Lundqvist.[9] The method has been used previously in crystalline calculations by Brinkman and Goodman,[10] who did the calculation for Si using $\rho^{1/3}$ rather than Hartree-Fock energy bands and the Penn-model[11] dielectric function, and by Lipari and Fowler,[12] who did the calculation for Ar using non-self-consistent approximate Hartree-Fock bands and the Penn model. In these two calculations the energies were computed only at symmetry points. In this paper, self-consistent exact Hartree-Fock energy bands are used and the energy shifts are calculated at general points in the Brillouin zone. Also, the calculation is done with the RPA dielectric function, the one actually called for in the SECH formalism, as well as with the Penn model. The method is applied to LiF using Euwema's Hartree-Fock bands.[2]

II. SCREENED-EXCHANGE PLUS COULOMB-HOLE APPROXIMATION

In this section we derive the SECH approximation. The results presented in the first part of the section, up to and including Eq. (8), are derived in detail in the Appendix by making use of the one-electron Green's function. For a crystal containing N electrons, the one-electron Green's function is defined by

$$\begin{aligned} G(xt, x't') &= -i\langle T[\psi(xt)\psi^\dagger(x't')]\rangle \\ &= -i[\langle\psi(xt)\psi^\dagger(x't')\rangle\Theta(t-t') \\ &\quad - \langle\psi^\dagger(x't')\psi(xt)\rangle\Theta(t'-t)] \, , \end{aligned} \tag{1}$$

$$\begin{aligned} \Theta(t-t') &= 1 \quad (t>t') \\ &= 0 \quad (t<t') \, , \end{aligned}$$

where $\langle\ \rangle$ denotes the expectation value with respect to the Heisenberg ground state of the N-particle system, T is the Dyson time-ordering operator, $\psi(xt)$ is the Heisenberg field operator, and x includes space and spin coordinates, $(x) = (\vec{r}, \xi)$.

The Green's function satisfies the equation

$$\begin{aligned} &\left(i\frac{\partial}{\partial t_1} - h(x_1) - V(x_1t_1)\right) G(x_1t_1, x_2t_2) - \int \Sigma(x_1t_1, x_3t_3) \\ &\quad \times G(x_3t_3, x_2t_2)\, dx_3\, dt_3 = \delta(x_1, x_2)\delta(t_1, t_2) \, , \end{aligned} \tag{2}$$

$$V(x_1t_1) = -i\int v(\vec{r}_1, \vec{r}_2) G(x_2t_1, x_2t_1^+)\, dx_2 \, , \tag{3}$$

$$v(\vec{r}_1, \vec{r}_2) = \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \, , \tag{4}$$

where h is the kinetic energy plus the interaction of the electron with the nuclei, e is the charge of an electron, $t^+ = t + \eta$ where $\lim_{\eta\to 0}$ is understood, and Σ is the self-energy which contains all the exchange and correlation effects.

If the self-energy is expanded in powers of the bare Coulomb interaction v and the first term of this expansion is used, then Eq. (2) becomes the Hartree-Fock equation which produces energy differences that are too large in comparison with experiment. More accurate results can be obtained by expressing the self-energy in powers of a screened interaction W which includes the effects of the polarization of the system. The first term of this expansion is given by

$$\Sigma(x_1t_1,\ x_2t_2)=iW(x_1t_1^+,\ x_2t_2)G(x_1t_1,\ x_2t_2)\ , \tag{5}$$

$$W(x_1t_1,\ x_2t_2)=\int v(\vec{r}_1,\ \vec{r}_3)\epsilon^{-1}(x_3t_1,\ x_2t_2)\,dx_3\ , \tag{6}$$

$$\epsilon(x_1t_1,\ x_2t_2)=\delta(x_1,\ x_2)\delta(t_1,\ t_2)-\int P(x_1t_1,\ x_3t_2)v(\vec{r}_3,\ \vec{r}_2)\,dx_3\ , \tag{7}$$

$$P(x_1t_1,\ x_2t_2)=-iG(x_1t_1,\ x_2t_2^+)G(x_2t_2,\ x_1t_1)\ , \tag{8}$$

where ϵ is the dielectric response function of the system and P is the irreducible polarization propagator.

When the Hamiltonian for the system is independent of time, it is easily seen that the Green's function depends only on the difference of the time arguments, in which case we can write G in terms of its Fourier transform:

$$G(x_1,\ x_2,\ t_1-t_2)=\frac{1}{2\pi}\int G(x_1,\ x_2,\ \omega)e^{-i\omega(t_1-t_2)}\,d\omega\ . \tag{9}$$

Then the Fourier transform of Eq. (2) is given by

$$[\omega-h(x_1)-V(x_1)]G(x_1,\ x_2,\ \omega)-\int\Sigma(x_1,\ x_3,\ \omega)G(x_3,\ x_2,\ \omega)\,dx_3=\delta(x_1,\ x_2)\ , \tag{10}$$

where

$$V(x_1)=\int v(\vec{r}_1,\ \vec{r}_3)\langle\rho(x_3)\rangle\,dx_3\ , \tag{11}$$

$$\rho(x)=\psi^\dagger(x)\psi(x)\ , \tag{12}$$

and $\psi(x)$ is the field operator in the Schrödinger representation.

In the expression for the self-energy given by (5), let us write the screened interaction as a bare part plus a part W_p due to polarization

$$W(x_1,\ x_2,\ \tau+\eta)=v(\vec{r}_1,\ \vec{r}_2)\delta(\tau+\eta)+W_p(x_1,\ x_2,\ \tau+\eta)\ ,$$

$$\tau=t_1-t_2\ .$$

It can be shown that $W_p(x_1,\ x_2,\ \tau)$ is a sharply peaked function of τ with the peak being symmetrical. Therefore we will approximate W_p in the above equation by its integrated value times a δ function; however, instead of $\delta(\tau+\eta)$ we will use $\delta(\tau)$ so as to pick up contributions from both parts of the Green's function. Then (5) becomes

$$\Sigma(x_1,\ x_2,\ \tau)=[\langle\psi(x_1)\psi^\dagger(x_2)\rangle\Theta(\tau)-\langle\psi^\dagger(x_2)\psi(x_1)\rangle\Theta(-\tau)]\times[v(\vec{r}_1,\ \vec{r}_2)\delta(\tau+\eta)+\int W_p(x_1,\ x_2,\ \tau')\times d\tau'\,\delta(\tau)]. \tag{13}$$

Since $\Theta(\tau)\delta(\tau)=\Theta(-\tau)\delta(\tau)=\frac{1}{2}\delta(\tau)$, the Fourier transform of (13) can be taken, yielding

$$\Sigma(x_1,\ x_2,\ \omega)=-\langle\psi^\dagger(x_2)\psi(x_1)\rangle v(\vec{r}_1,\ \vec{r}_2)+\tfrac{1}{2}[\langle\psi(x_1)\psi^\dagger(x_2)\rangle-\langle\psi^\dagger(x_2)\psi(x_1)\rangle]W_p(x_1,\ x_2,\ \omega=0)\ , \tag{14}$$

where

$$\int W_p(x_1,\ x_2,\ \tau')\,d\tau'=W_p(x_1,\ x_2,\ \omega=0)\ .$$

Inside the brackets in Eq. (14) we add and subtract the second term to obtain

$$\Sigma_{\mathrm{SECH}}(x_1,x_2)=-\langle\rho(x_1,x_2)\rangle W(x_1,x_2,\omega=0)+\tfrac{1}{2}\delta(x_1,x_2)[W(x_1,x_2,\omega=0)-v(\vec{r}_1,\vec{r}_2)]\ , \tag{15}$$

where

$$\begin{aligned}\rho(x_1,\ x_2)&=\psi^\dagger(x_2)\psi(x_1)\ ,\\ W(x_1,\ x_2,\ \omega)&=v(\vec{r}_1,\ \vec{r}_2)+W_p(x_1,\ x_2,\ \omega)\ .\end{aligned} \tag{16}$$

In the expression for Σ_{SECH} the first term leads to a statically screened exchange (SE), while the second produces a Coulomb hole (CH).

In this approximation Σ is independent of ω. When this is the case, we can solve the following equation self-consistently to obtain a complete orthonormal set of one-electron states u_k with corresponding energies ϵ_k:

$$[h(x_1)+V(x_1)]u_k(x_1)+\int\Sigma(x_1,\ x_3)u_k(x_3)\,dx_3=\epsilon_k u_k(x_1)\ . \tag{17}$$

If we subtract the term $\omega u_k(x_1)$ from both sides of this equation, multiply both sides by $u_k^*(x_2)/(\epsilon_k-\omega)$, sum over k, and compare with Eq. (10), we obtain for the Green's function

$$G(x_1,\ x_2,\ \omega)=\sum_k\frac{u_k(x_1)u_k^*(x_2)}{\omega-\epsilon_k}\ . \tag{18}$$

By comparing (18) with the general expression for the Fourier transform of the Green's function, which can be obtained from (1), we have

$$\begin{aligned}&\epsilon_k\to\epsilon_k+i\delta,\quad k\text{ occupied}\\ &\epsilon_k\to\epsilon_k-i\delta,\quad k\text{ unoccupied}\end{aligned} \tag{19}$$

where $\lim_{\delta\to0}$ is understood. The energies ϵ_k are unrelaxed ionization energies and unrelaxed electron affinities for k occupied and unoccupied, respectively. Comparing (18) with the general Fourier transform of the Green's function, we see that when Σ is independent of frequency, the density matrix is given by

$$\langle\rho(x_1,\ x_2)\rangle = \sum_{k\ \mathrm{occ}} u_k(x_1)u_k^*(x_2)\ . \tag{20}$$

Using (8), the Fourier transform of the polarization can be written

$$P(x_1,\ x_2,\ \omega) = -\frac{i}{2\pi}\int G(x_1,\ x_2,\ \omega') \times G(x_2,\ x_1,\ \omega'-\omega)e^{i\omega'\eta}\,d\omega'$$

and, using (18) and (19), this becomes

$$P(x_1, x_2, \omega) = \sum_{kk'} \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'} - \omega} u_k(x_1)u_k{}^*(x_2)u_{k'}^*(x_1)u_{k'}(x_2), \tag{21}$$

where n_k is the occupation number (either 0 or 1) of the state u_k.

III. ENERGY SHIFTS

If the self-energy were given by

$$\Sigma_{\mathrm{HF}}(x_1,\ x_2) = -\langle\rho(x_1,\ x_2)\rangle v(\vec{r}_1,\ \vec{r}_2)\ , \tag{22}$$

then (17) 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 $u_{\vec{k}l}$ and $\epsilon_{\vec{k}l}$, respectively, where $\vec{k}$ is a reciprocal space vector restricted to the first zone and l 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 $\Delta\epsilon_{\vec{k}l}$ to the HF energies due to using Σ_{SECH} in Eq. (17). Considering the HF Hamiltonian to be unperturbed and letting the difference between Σ_{SECH} and Σ_{HF} be the perturbation, the first-order correction to the energy is then given by

$$\begin{aligned}\Delta\epsilon_{\vec{k}l} &= \int u_{\vec{k}l}^*(x_1)[\Sigma_{\mathrm{SECH}}(x_1,\ x_2) - \Sigma_{\mathrm{HF}}(x_1,\ x_2)]u_{\vec{k}l}(x_2)\,dx_1\,dx_2\\ &= -\int u_{\vec{k}l}^*(x_1)\langle\rho(x_1, x_2)\rangle[W(x_1, x_2, \omega=0) - v(\vec{r}_1, \vec{r}_2)]u_{\vec{k}l}(x_2)\,dx_1\,dx_2\\ &\quad + \frac{1}{2}\int u_{\vec{k}l}^*(x_1)\delta(x_1, x_2)[W(x_1, x_2, \omega=0) - v(\vec{r}_1, \vec{r}_2)]u_{\vec{k}l}(x_2)\,dx_1\,dx_2\ .\end{aligned} \tag{23}$$

The first part of the above expression is the difference between a screened- and unscreened-exchange term, while the second part is a Coulomb-hole term. These energy shifts $\Delta\epsilon_{\vec{k}l}$, which are correlation corrections, have been obtained by using Green's-function theory to go beyond the HF approximation.

For a spin-independent problem, the integration over the spin coordinates in (23) can be carried out. Then, writing the bare and screened interactions in terms of their Fourier transforms, we have

$$v(\vec{r}_1,\ \vec{r}_2) = \frac{1}{(2\pi)^3}\int v(\vec{q})e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)}\,d\vec{q}\ , \tag{24}$$

$$W(\vec{r}_1,\ \vec{r}_2, \omega) = \frac{1}{(2\pi)^6}\int W(\vec{q}, \vec{q}\,', \omega)e^{i\vec{q}\cdot\vec{r}_1 - i\vec{q}\,'\cdot\vec{r}_2}\,d\vec{q}\,d\vec{q}\,'\ , \tag{25}$$

where

$$W(\vec{q},\ \vec{q}\,', \omega) = v(\vec{q})\epsilon^{-1}(\vec{q}, \vec{q}\,', \omega), \quad v(\vec{q}) = 4\pi e^2/q^2, \tag{26}$$

$$\epsilon(\vec{q},\ \vec{q}\,',\ \omega) = (2\pi)^3\delta(\vec{q},\ \vec{q}\,') - P(\vec{q},\ \vec{q}\,',\ \omega)v(\vec{q}\,')\ . \tag{27}$$

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

$$u_{\vec{k}l}(\vec{r}) = \frac{1}{\sqrt{N_c}}\sum_{i\nu} b_{li}(\vec{k})e^{i\vec{k}\cdot\vec{R}_\nu}\phi_i(\vec{r} - \vec{R}_\nu)\ , \tag{28}$$

where the sums are over atomic orbitals ϕ_i and direct-lattice vectors $\vec{R}_\nu$, the b_{li}'s are the coefficients of the Bloch functions associated with the atomic orbitals, and N_c is the number of unit cells in the crystal. The δ function is related to a sum over direct-lattice vectors as follows:

$$\frac{(2\pi)^3}{\Omega}\sum_{\vec{K}} \delta(\vec{k} - \vec{K}) = \sum_{\nu} e^{i\vec{k}\cdot\vec{R}_\nu}\ , \tag{29}$$

where the sum on the left-hand side is over reciprocal-lattice vectors $\vec{K}$ and Ω is the volume of the unit cell. Using (28) and (29), (27) becomes

$$\epsilon(\vec{q},\ \vec{q}\,',\ \omega) = (2\pi)^3\delta(\vec{q},\ \vec{q}\,') - \sum_{\vec{K}_2} P'(\vec{q},\ \vec{q} + \vec{K}_2,\ \omega)v(\vec{q} + \vec{K}_2) \times \delta(\vec{q} + \vec{K}_2,\ \vec{q}\,'), \tag{30}$$

where the sum is over reciprocal-lattice vectors $\vec{K}_2$ and P' is given by

$$\begin{aligned}P'(\vec{q}, \vec{q} + \vec{K}_2, \omega) = \frac{2(2\pi)^3}{V_c}\sum_{\vec{k}ll'} &\frac{n_{\vec{k}+\vec{q}+\vec{K}_1, l} - n_{\vec{k}l'}}{\epsilon_{\vec{k}+\vec{q}+\vec{K}_1, l} - \epsilon_{\vec{k}l'} - \omega}\\ &\times\langle\vec{k}l'\,|e^{-i\vec{q}\cdot\vec{r}_1}|\,\vec{k} + \vec{q} + \vec{K}_1, l\rangle\\ &\times\langle\vec{k}l'\,|e^{-i(\vec{q}+\vec{K}_2)\cdot\vec{r}_2}|\,\vec{k} + \vec{q} + \vec{K}_1, l\rangle^*\ .\end{aligned} \tag{31}$$

The factor of 2 in front of the sum is due to spin, V_c is the volume of the crystal, $\vec{K}_1$ is the reciprocal-lattice vector such that $\vec{k} + \vec{q} + \vec{K}_1$ is in the first zone, and $|\vec{k}l\rangle = u_{\vec{k}l}$.

The dielectric function given by (30) is known as the random-phase-approximation (RPA) dielectric function. Wiser[13] has shown that in many cases the effect of the off-diagonal terms of the RPA dielectric matrix is small. Therefore we make the approximation of keeping only the $\vec{K}_2 = 0$ term in (30), in which case ϵ becomes

$$\epsilon(\vec{q}, \vec{q}', \omega) = [(2\pi)^3 - P'(\vec{q}, \vec{q}, \omega) v(\vec{q})]\delta(\vec{q}, \vec{q}') , \quad (32)$$

where

$$P'(\vec{q},\vec{q},\omega) = \frac{2(2\pi)^3}{V_c} \sum_{\vec{k}ll'} \frac{n_{\vec{k}+\vec{q}+\vec{K}_1, l} - n_{\vec{k}l'}}{\epsilon_{\vec{k}+\vec{q}+\vec{K}_1, l} - \epsilon_{\vec{k}l'} - \omega} \times |\langle \vec{k}l' | e^{-i\vec{q}\cdot\vec{r}_1} | \vec{k}+\vec{q}+\vec{K}_1, l\rangle|^2 . \quad (33)$$

The inverse is then readily obtained:

$$\epsilon^{-1}(\vec{q},\vec{q}',\omega) = \frac{(2\pi)^3}{\epsilon(\vec{q},\omega)} \delta(\vec{q},\vec{q}') , \quad (34)$$

$$\epsilon(\vec{q},\omega) = 1 - \frac{1}{(2\pi)^3} v(\vec{q}) P'(\vec{q},\vec{q},\omega) . \quad (35)$$

Combining (34), (26), and (25), we have

$$W(\vec{r}_1, \vec{r}_2, \omega) = \frac{1}{(2\pi)^3} \int \frac{v(\vec{q})}{\epsilon(\vec{q},\omega)} e^{i\vec{q}\cdot(\vec{r}_1 - \vec{r}_2)} d\vec{q} . \quad (36)$$

Then, using (24) and (36), the energy shifts become

$$\Delta\epsilon_{\vec{k}l} = -\frac{1}{(2\pi)^3} \int u^*_{\vec{k}l}(\vec{r}_1) \rho(\vec{r}_1, \vec{r}_2) v(\vec{q}) \left(\frac{1}{\epsilon(\vec{q}, \omega=0)} - 1\right) \times e^{i\vec{q}\cdot(\vec{r}_1-\vec{r}_2)} u_{\vec{k}l}(\vec{r}_2)\, d\vec{r}_1\, d\vec{r}_2\, d\vec{q} + \frac{1}{2}\frac{1}{(2\pi)^3} \int v(\vec{q}) \times \left(\frac{1}{\epsilon(\vec{q}, \omega=0)} - 1\right) d\vec{q} , \quad (37)$$

where

$$\rho(\vec{r}_1, \vec{r}_2) = \sum_{\vec{k}', l' \ \text{occ}} u_{\vec{k}'l'}(\vec{r}_1) u^*_{\vec{k}'l'}(\vec{r}_2) . \quad (38)$$

Using (28), (29), and (38), (37) becomes

$$\Delta\epsilon_{\vec{k}l} = -\frac{1}{V_c} \sum_{\vec{K}, \vec{k}', l' \ \text{occ}} |\langle \vec{k}'l' | \times e^{-i(\vec{k}-\vec{k}'+\vec{K})\cdot\vec{r}} | \vec{k}l\rangle|^2 v(\vec{k}-\vec{k}'+\vec{K}) \times \left(\frac{1}{\epsilon(\vec{k}-\vec{k}'+\vec{K}, \omega=0)} - 1\right) + \frac{1}{2}\frac{1}{(2\pi)^3} \int v(\vec{q}) \times \left(\frac{1}{\epsilon(\vec{q}, \omega=0)} - 1\right) d\vec{q} , \quad (39)$$

where the sum on $\vec{K}$ is over reciprocal-lattice vectors. Making the approximation that the dielectric function $\epsilon(\vec{q}, \omega=0)$ falls off to 1 outside 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 (39) to the first zone. Since the factor $1/\epsilon - 1$ appears in both terms of (39), the above approximation neglects positive and negative terms which, in addition to being small, cancel each other to some extent.

IV. RESULTS FOR LiF

The energy shifts described above have been calculated for LiF using the LCAO HF energy bands of Euwema *et al.*[2] The energies $\epsilon_{\vec{k}l}$ and wave functions $u_{\vec{k}l}$ were initially determined at 20 points in $\frac{1}{48}$ of the Brillouin zone, and then the coefficients b_{il} in (28) were permuted to obtain the $u_{\vec{k}l}$'s at 341 points throughout the zone. Using these 341 points in the sum over $\vec{k}'$ in (39), the energy shifts $\Delta\epsilon_{\vec{k}l}$ were computed for the six occupied bands and first eight conduction bands at 20 points in $\frac{1}{48}$ of the zone.

The dielectric function that appears in this method is the one given by (32), which is also known as the diagonal part of the RPA dielectric function. Since we are using first-order perturbation theory to obtain the energy shifts, the dielectric function must be computed with the HF energies and wave functions. For this calculation, the six occupied bands and first eight conduction bands were used, with the $\vec{k}$ summation in (33) being carried out over 341 zone points. The RPA appears to be fairly well converged after eight conduction bands, as indicated by Table I.

Figure 1 shows a comparison between 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[11] dielectric function, where the latter is a semiempirical model that takes on the experimental value for the optical dielectric constant when $\vec{q}=0$. We see that the HF RPA is quite a bit smaller than the experimental value as represented by the Penn model. This is due partly to the fact that the uncorrelated HF energy differences, which appear in the denominator of (33), are too large; however, the SECH RPA shows that correcting the HF energy differences produces only a small change. Other factors contributing to the difference between the HF RPA and experiment are the uncorrelated wave functions used in the matrix elements in (33), 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 (30)] which correspond to local field effects. Since the Penn-model dielectric function matches experiment, it was used to obtain the SECH correlation corrections. Energy shifts were

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

Bands	$\epsilon(\vec{q}, 0)$
1	1.121
2	1.167
3	1.206
4	1.244
5	1.250
6	1.253
7	1.255
8	1.258

also computed using the diagonal part of the HF RPA so that a comparison could be made between the Penn-model and HF RPA results.

The energy shifts given in (39) are state dependent due to the first term, which is the difference between a screened and unscreened exchange, while the second term, the Coulomb hole, is constant in the approximation for the dielectric function given by (32). If the full dielectric matrix as given in (30), rather than just the diagonal part, is used, then the Coulomb-hole term is also state dependent. For core and valence bands, the first term in (39) is larger than the second, giving positive energy shifts, while for conduction bands the Coulomb-hole term is larger and the energy shifts are negative. Therefore these correlation corrections raise the occupied bands and lower the conduction bands with a resulting decrease in energy differences.

Figure 2 gives the uncorrelated HF energy bands which yield energy differences that are too large in comparison with experiment. Table II shows the SECH correlation corrections for the top valence and bottom conduction bands and the corresponding band-gap changes, obtained with the Penn-model dielectric function. We see that as one moves out from the center of the zone along the Δ, Σ, and Λ axes, there is an increase in the gap changes which tends to flatten the bands; however, these gap changes do not vary over the zone by more than one-quarter of an eV. The last column of Table II gives the band-gap changes obtained with the diagonal part of the HF RPA dielectric function, and it is seen that the HF RPA produces less than half of

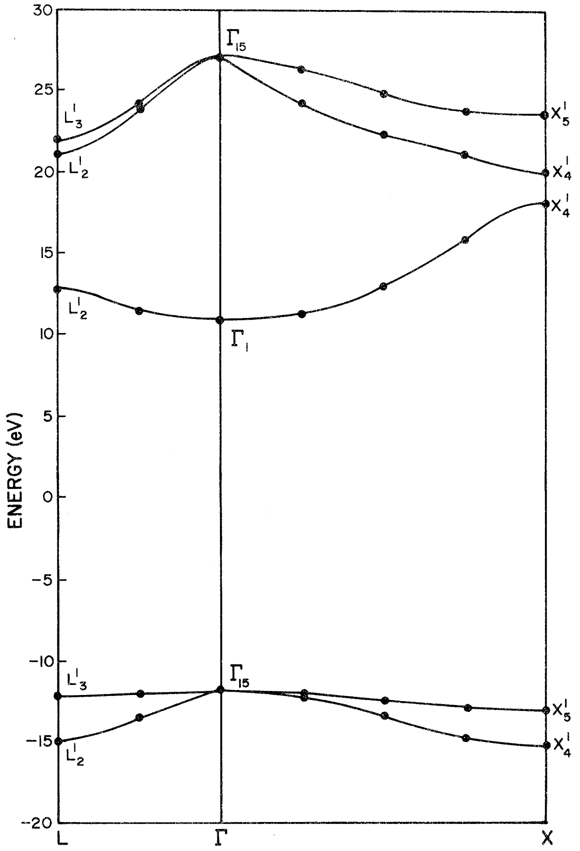

FIG. 2. Uncorrelated HF energy bands for LiF.

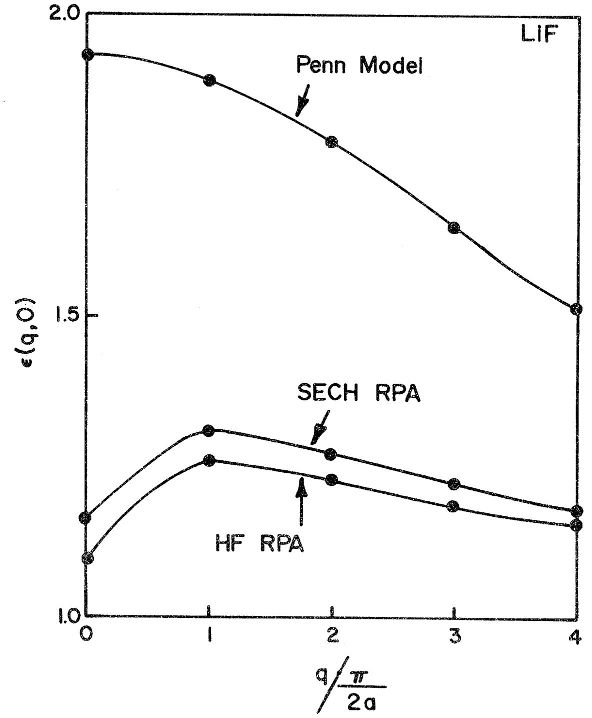

FIG. 1. LiF dielectric functions along the Δ axis from the center of the zone to the zone boundary $2\pi/a$, where a is the lattice constant.

TABLE II. SECH energy shifts for LiF at several points $\vec{q}$ in the first zone. $\Delta\epsilon_v$ is the top valence-band shift, $\Delta\epsilon_c$ is the bottom conduction-band shift, and $\Delta E_g^{(\text{Penn})}$ is the corresponding band-gap change, obtained with the Penn model. $\Delta E_g^{(\text{HF RPA})}$ is the band-gap change computed with the HF RPA. Shifts and gap changes are in eV.

	$\vec{q}$	$\Delta\epsilon_v$	$\Delta\epsilon_c$	$\Delta E_g^{(\text{Penn})}$	$\Delta E_g^{(\text{HF RPA})}$
$(\pi/2a)$	(0, 0, 0)	2.39	−2.62	5.01	1.87
	(1, 0, 0)	2.39	−2.63	5.02	1.88
	(2, 0, 0)	2.41	−2.67	5.08	1.90
	(3, 0, 0)	2.43	−2.74	5.17	1.95
	(4, 0, 0)	2.44	−2.80	5.24	1.98
	(1, 1, 0)	2.38	−2.65	5.03	1.88
	(2, 2, 0)	2.39	−2.70	5.09	1.91
	(3, 3, 0)	2.42	−2.75	5.17	1.94
	(1, 1, 1)	2.39	−2.66	5.05	1.89
	(2, 2, 2)	2.39	−2.69	5.08	1.91

the correlation obtained with the Penn model.

Figure 3 gives the SECH correlated energy bands, while Table III compares the corresponding SECH correlated energy differences, obtained with the Penn model, to the uncorrelated HF band gaps at a few symmetry points. We see that the SECH correlation correction reduces the HF band gap at Γ from 22.9 to 17.9 eV, compared with the experimental value of 13.6 eV.[14] Thus the SECH method provides over half of the correlation needed in LiF for the top of the valence band.

An additional correlation correction, due to relaxation effects, is important in alkali halides and needs to be included along with the SECH energy shifts in order to describe excitations of the N-electron system. If this correction is treated in the approximate manner of Mickish *et al.*,[4] then an additional gap change at Γ of 4.6 eV is obtained. This reduces the fundamental band gap to 13.3 eV, which is in close agreement with experiment.

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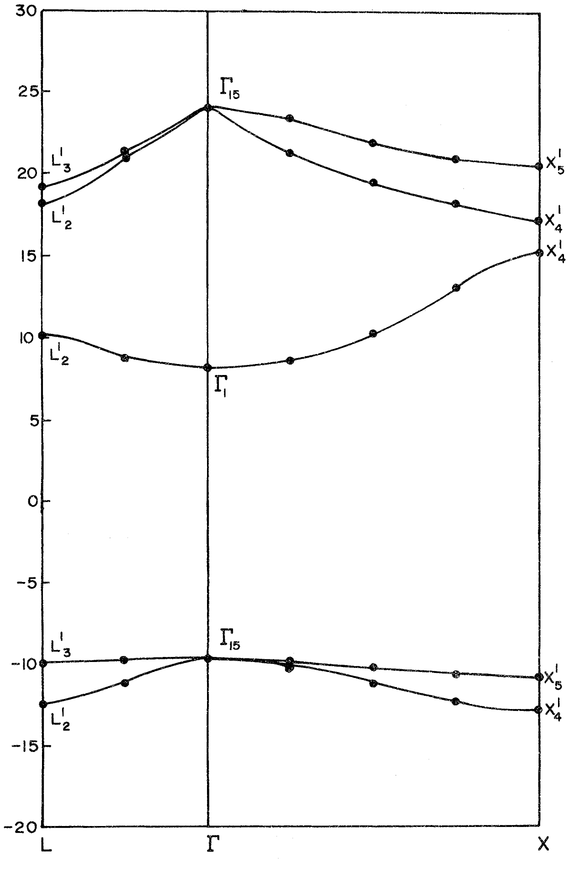

FIG. 3. SECH correlated energy bands for LiF.

TABLE III. LiF HF and SECH band gaps in eV.

	HF	SECH
$\Gamma_{15}\to\Gamma_1$	22.9	17.9
$X'_5\to X'_4$	31.2	26.0
$L'_3\to L'_2$	25.0	19.9

APPENDIX A: BASIC FORMALISM

In deriving the expression for the energy shifts in the SECH method, we follow closely the work of Hedin and Lundqvist,[9] who formulated the problem in terms of Green's functions. Consider a small external potential acting on a neutral crystal containing N electrons. Then in the linear approximation the Hamiltonian is given by

$$H=\sum_i h(x_i)+\frac{1}{2}\sum_{i\neq j} v(\vec{r}_i,\ \vec{r}_j)+\sum_i \phi(x_i t)+V_{\text{nuclear}}\ . \tag{A1}$$

The sums are over electronic coordinates x_i, where x includes space and spin coordinates, $(x)=(\vec{r},\xi)$, h is the kinetic energy plus the interaction of the electron with the nuclei, v is the Coulomb interaction given by

$$v(\vec{r}_i,\ \vec{r}_j)=\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\ ,$$

where e is the charge of an electron, V_{nuclear} is the Coulomb repulsion of the nuclei which is treated as a constant here, and ϕ is the external potential which is introduced in order to derive an expression for the dielectric response function. After the final equations have been obtained, ϕ will be set equal to zero.

Now let us introduce the field operator $\psi(x)$ which satisfies the following anticommutation relations:

$$\{\psi(x),\psi(x')\}=\{\psi^\dagger(x),\psi^\dagger(x')\}=0\ ,$$

$$\{\psi(x),\psi^\dagger(x')\}=\delta(x,x')\ .$$

Then the Hamiltonian can be written in second-quantized form as follows:

$$H(t)=\int\psi^\dagger(x)h(x)\psi(x)dx+\frac{1}{2}\int\psi^\dagger(x)\psi^\dagger(x')v(\vec{r},\vec{r}\,')\psi(x')\psi(x)\,dx\,dx'+\int\psi^\dagger(x)\psi(x)\phi(xt)\,dx+V_{\text{nuclear}} \tag{A2}$$

$$=H_0+H_1(t)\ , \tag{A3}$$

$$H_1(t)=\int\rho(x)\phi(xt)\,dx\ , \tag{A4}$$

$$\rho(x) = \psi^\dagger(x)\psi(x) \; . \tag{A5}$$

Let $|t\rangle$ be the state of the N-particle system at time t. Then the time-evolution operator U is defined by

$$|t\rangle = U(tt')\,|t'\rangle \; ,$$

where

$$U(tt) = 1 \; , \tag{A6}$$

$$U(t_1t_2) = U(t_1t_3)U(t_3t_2) \; . \tag{A7}$$

Applying the Schrödinger equation

$$H(t)\,|t\rangle = i\frac{\partial}{\partial t}\,|t\rangle \; ,$$

we have

$$i\frac{\partial}{\partial t}U(tt') = H(t)U(tt') \; . \tag{A8}$$

Also the time-evolution operator for H_0 satisfies

$$i\frac{\partial}{\partial t}U_0(tt') = H_0U_0(tt') \; , \tag{A9}$$

where

$$U_0(tt') = e^{-iH_0(t-t')} \; , \tag{A10}$$

$$U_0^\dagger(tt') = U_0(t't) \; . \tag{A11}$$

Equations (A8) and (A9) can be combined to obtain an integral equation for the time-evolution operator

$$U(t_1t_2) = U_0(t_1t_2) - i\int_{t_2}^{t_1} U_0(t_1t_3)H_1(t_3)U(t_3t_2)\,dt_3 \; . \tag{A12}$$

Taking the functional derivative of both sides with respect to the external potential and using Eq. (A4), we have

$$\begin{aligned}\int_{t_2}^{t_1}[2\delta(t_1,\; t_3) + iU_0(t_1t_3)H_1(t_3)]\frac{\delta U(t_3t_2)}{\delta\phi(x_4t_4)}\,dt_3 &= -\,iU_0(t_1t_4)\rho(x_4)U(t_4t_2) \quad (t_1 > t_4 > t_2)\\ &= 0 \qquad (t_4 > t_1,\quad t_4 < t_2) \; ,\end{aligned} \tag{A13}$$

which implies that

$$\frac{\delta U(t_1t_2)}{\delta\phi(x_4t_4)} = 0 \; , \quad t_4 > t_1, \quad t_4 < t_2 \; . \tag{A14}$$

Therefore we can change the lower limit of integration in Eq. (A13) to t_4. Solving Eq. (A12) for $U_0(t_1t_4)$, substituting this into the right-hand side of (A13), comparing the integrands of both sides, and using (A14) yields

$$\begin{aligned}\frac{\delta U(t_1t_2)}{\delta\phi(x_3t_3)} &= -\,iU(t_1t_3)\rho(x_3)U(t_3t_2) \quad (t_1 > t_3 > t_2)\\ &= 0 \qquad (t_3 > t_1,\quad t_3 < t_2) \; .\end{aligned} \tag{A15}$$

Define an operator O_H in the Heisenberg representation by

$$O_H(t) = U(t_0t)\,O_S\,U(tt_0) \; , \quad t_0 \to -\infty \tag{A16}$$

where O_S is the corresponding Schrödinger operator. In this case the equivalence of the Heisenberg and Schrödinger pictures occurs at t_0:

$$O_H(t_0) = O_S \; ,$$

$$|\Psi_S(t_0)\rangle = |\Psi_H\rangle \; ,$$

where $|\Psi_S\rangle$ and $|\Psi_H\rangle$ are Schrödinger and Heisenberg states, respectively. Also define the ground-state expectation value of a time-ordered product of Heisenberg operators as

$$\langle T[O_1(t_1)O_2(t_2)\cdots]\rangle = \frac{\langle N|\,U_0(t_0,\; -t_0)U(-t_0,\; t_0)T[O_1(t_1)O_2(t_2)\cdots]\,|N\rangle}{\langle N|\,U_0(t_0,\; -t_0)U(-t_0,\; t_0)\,|N\rangle} \; , \tag{A17}$$

where $|N\rangle$ is the Heisenberg ground state of the N-particle system. Then, using Eqs. (A15) and (A17), we have

$$\begin{aligned}\frac{\delta\langle T[O_1(t_1)O_2(t_2)\cdots]\rangle}{\delta\phi(xt)} &= -\,i\langle T[\rho(xt)O_1(t_1)O_2(t_2)\cdots]\rangle\\ &\quad + i\langle\rho(xt)\rangle\langle T[O_1(t_1)O_2(t_2)\cdots]\rangle \; ,\end{aligned} \tag{A18}$$

$$\rho(xt) = \psi^\dagger(xt)\psi(xt) \; , \qquad \psi(xt) = U(t_0t)\psi(x)U(tt_0) \; . \tag{A19}$$

The Heisenberg field operator satisfies the Heisenberg equation of motion

$$i\frac{\partial}{\partial t}\psi(xt) = [\psi(xt), H(t)]$$

and, using (A2), this becomes

$$\begin{aligned}i\frac{\partial}{\partial t}\psi(xt) &= [h(x) + \phi(xt)]\psi(xt)\\ &\quad + \int v(\vec{r}, \vec{r}\,'')\psi^\dagger(x''t)\psi(x''t)\psi(xt)\,dx'' \; .\end{aligned} \tag{A20}$$

Define the one-electron Green's function as

$$\begin{aligned}G(xt, x't') &= -\,i\langle T[\psi(xt)\psi^\dagger(x't')]\rangle\\ &= -\,i[\langle\psi(xt)\psi^\dagger(x't')\rangle\Theta(t-t')\\ &\quad - \langle\psi^\dagger(x't')\psi(xt)\rangle\Theta(t'-t)] \; ,\end{aligned} \tag{A21}$$

$$\Theta(t-t') = 1 \quad (t > t')$$

$$=0 \quad (t<t') .$$

Using the relation

$$\frac{\partial}{\partial t}\Theta(t-t')=\delta(tt') ,$$

we have

$$i\frac{\partial}{\partial t}G(xt,x't')=\left\langle T\left(\frac{\partial}{\partial t}\psi(xt)\psi^\dagger(x't')\right)\right\rangle+\delta(x,x')\delta(t,t'). \tag{A22}$$

Multiplying Eq. (A20) on the right-hand side by $\psi^\dagger(x't')$, taking the time-ordered product and ground-state expectation value of both sides, and using (A22), we have

$$\left(i\frac{\partial}{\partial t}-h(x)-\phi(xt)\right)G(xt,\ x't')+i\int v(\vec{r},\vec{r}'')\delta(t+\eta,\ t'')\langle T[\psi^\dagger(x''t'')\psi(x''t'')\psi(xt)\psi^\dagger(x't')]\rangle \times dx''\,dt''=\delta(x,\ x')\delta(t,\ t') , \tag{A23}$$

where we have inserted a δ function and integration over t'' in the second term on the left and $\lim_{\eta\to 0}$ is understood. Using the notation

$$(1)=(x_1,\ t_1),\quad (1^+)=(x_1,\ t_1+\eta),$$

$$v(12)=v(\vec{r}_1,\ \vec{r}_2)\delta(t_1,\ t_2),$$

$$\delta(12)=\delta(x_1,\ x_2)\delta(t_1,\ t_2),$$

we can write (A23) as

$$\left(i\frac{\partial}{\partial t_1}-h(x_1)-\phi(1)\right)G(12)+i\int v(1^+3)\times\langle T[\rho(3)\psi(1)\psi^\dagger(2)]\rangle\, d(3)=\delta(12)$$

and using (A18) this becomes

$$\left(i\frac{\partial}{\partial t_1}-h(x_1)-V(1)\right)G(12)-i\int v(1^+3)\frac{\delta G(12)}{\delta\phi(3)}d(3)=\delta(12) , \tag{A24}$$

$$V(1)=\phi(1)+\int v(13)\langle\rho(3)\rangle d(3) . \tag{A25}$$

Using the definition of the Green's function, $V(1)$ becomes

$$V(1)=\phi(1)-i\int v(13)G(33^+)d(3) . \tag{A26}$$

Define the screened interaction W by

$$W(12)=\int v(13)\epsilon^{-1}(32)d(3) , \tag{A27}$$

where the dielectric response function ϵ is defined as

$$\epsilon(12)=\frac{\delta\phi(2)}{\delta V(1)}=\delta(12)+i\int v(23)\frac{\delta G(33^+)}{\delta V(1)}d(3) . \tag{A28}$$

Then define the irreducible polarization propagator P by

$$\epsilon(12)=\delta(12)-\int P(13)v(32)d(3) , \tag{A29}$$

so that

$$P(12)=-i\frac{\delta G(22^+)}{\delta V(1)} =i\int G(23)\frac{\delta G^{-1}(34)}{\delta V(1)}G(42^+)d(34) , \tag{A30}$$

where we have used the identity

$$\frac{\delta G(12)}{\delta V(3)}=-\int G(14)\frac{\delta G^{-1}(45)}{\delta V(3)}G(52)d(45) . \tag{A31}$$

From (A29) and (A27), the inverse of the dielectric function is

$$\epsilon^{-1}(12)=\delta(12)+\int P(13)W(32)d(3) ,$$

so that (A27) becomes

$$W(12)=v(12)+\int v(13)P(34)W(42)d(34) . \tag{A32}$$

Let us write the second term on the left-hand side of (A24) as

$$-i\int v(1^+4)\frac{\delta G(12)}{\delta V(3)}\frac{\delta V(3)}{\delta\phi(4)}d(34) .$$

Then, using the relation

$$\epsilon^{-1}(43)=\frac{\delta V(3)}{\delta\phi(4)}$$

and (A27), the second term in (A24) becomes

$$-i\int W(1^+3)\frac{\delta G(12)}{\delta V(3)}d(3)$$

and, using (A31), this becomes

$$i\int W(1^+3)G(14)\frac{\delta G^{-1}(45)}{\delta V(3)}G(52)d(345) .$$

Defining the self-energy Σ as

$$\Sigma(12)=-i\int W(1^+3)G(14)\frac{\delta G^{-1}(42)}{\delta V(3)}d(34) , \tag{A33}$$

Eq. (A24) becomes

$$\left(i\frac{\partial}{\partial t_1}-h(x_1)-V(1)\right)G(12)-\int\Sigma(13)G(32)d(3)=\delta(12) . \tag{A34}$$

Define the vertex function Γ by

$$\Gamma(12,3) = -\frac{\delta G^{-1}(12)}{\delta V(3)} . \tag{A35}$$

Multiplying (A34) on the right-hand side by $G^{-1}(24)$ and integrating over 2, we have

$$\left(i\frac{\partial}{\partial t_1} - h(x_1) - V(1)\right)\delta(14) - \Sigma(14) = G^{-1}(14) ,$$

so that Γ becomes

$$\begin{aligned}\Gamma(12,3) &= \delta(12)\delta(13) + \frac{\delta\Sigma(12)}{\delta V(3)} \\ &= \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)}\frac{\delta G(45)}{\delta V(3)} d(45) ,\end{aligned}$$

and, using (A31) and (A35), this becomes

$$\begin{aligned}\Gamma(12,3) = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)\Gamma(67,3) \\ \times G(75) d(4567) .\end{aligned} \tag{A36}$$

Putting (A35) into (A33) and (A30), we have

$$\Sigma(12) = i\int W(1^+3)G(14)\Gamma(42,3)d(34) , \tag{A37}$$

$$P(12) = -i\int G(23)\Gamma(34,1)G(42^+)d(34) . \tag{A38}$$

The last three equations together with Eq. (A32) can be iterated to obtain successively more accurate approximations for Σ as a functional of G. The expression for Σ so obtained can then be put into Eq. (A34), yielding a self-consistent equation for the Green's function.

If we use $\Sigma = 0$ as a starting point, then Γ becomes

$$\Gamma(12,3) = \delta(12)\delta(13) \tag{A39}$$

and this yields a new expression for Σ,

$$\Sigma(12) = iW(1^+2)G(12) , \tag{A40}$$

with a corresponding expression for P

$$P(12) = -iG(12^+)G(21) . \tag{A41}$$

Since the iterations become increasingly more complicated, we will stop at this point and use the approximation for Σ given by (A40). This is the first term of an expansion for Σ in powers of a screened, rather than bare, interaction. This approximation for Σ neglects vertex corrections due to the simple expression given for the vertex function in Eq. (A39).

Now that the final equations have been obtained, we set the external potential equal to zero, in which case the dielectric function becomes a linear response function. Since $\phi = 0$, $H(t) = H_0 \Rightarrow U = U_0$ and the ground-state expectation value defined in (A17) takes the usual form,

$$\langle T[O_1(t_1)O_2(t_2)\cdots]\rangle = \langle N|T[O_1(t_1)O_2(t_2)\cdots]|N\rangle .$$

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