Ground- and excited-state properties of LiF in the local-density formalism*

Alex Zunger

Department of Physics and Astronomy, and the Materials Research Center, Northwestern University, Evanston, Illinois 60201

A. J. Freeman

Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201 and Argonne National Laboratory, Argonne, Illinois 60439 (Received 2 May 1977)

The band structure, charge density, x-ray scattering factor (and their behavior under pressure), equilibrium lattice constant, and cohesive energy of the prototype ionic solid LiF were determined using our recently developed self-consistent numerical basis set (non-muffin-tin) linear-combination-of-atomic-orbitals method, within the local-density formalism (LDF). The details of the bonding and the effects of exchange and correlation on the electronic structure are discussed with reference to the conventional picture of ionic bonding. Remarkably good agreement is found with the observed data for the ground-state properties of the system. Contrary to the results of previous band studies, the conventional band-structure approach to excitation energies (i.e., identifying them with the band eigenvalue differences) is found to fail completely in accounting for the observed data in the entire x-ray and optical spectral region when fully self-consistent solutions of the LDF one-particle equation with no further approximation to the crystal potential are obtained. It is found that in the presence of some spatial localization of the initial or final crystal states, the spurious self-interaction terms, as well as the polarization and orbital relaxation self-energy effects are of a similar order of magnitude as the Koopmans'-like interband terms. In order to treat these effects within the LDF self-consistently, we describe the excitation processes as transitions involving point-defect-like states in the solid calculated by a supercell method in which the excitation energies are determined as total-energy differences between (separately calculated) excited- and ground-state configurations. The excited state is represented as a superlattice of locally excited sites using large (8- and 16- atom) unit cells, each containing a single excited site. We find, in the self-consistency limit, that a small but finite degree of spatial localization of the excited states exists even for valence excitations, inducing thereby self-interaction as well as self-energy relaxation and polarization effects. The LDF model is found to account very well for both interband and exciton transitions over the entire spectral region (12-695 eV) and to yield definite predictions regarding the exciton bandwidths and series limits.

I. INTRODUCTION

The study of the ground-state electronic properties of molecules and solids in the local-density formalism (LDF)¹⁻³ has recently attracted considerable attention. Investigations of the cohesive properties of small molecules,⁴⁻⁶ metals,^{7,8} and rare-gas solids⁹ have elucidated the possibilities of obtaining a reasonably accurate description of binding energies and equilibrium geometries by incorporating exchange and correlation effects directly into a one-body potential. Similar studies on compounds, ionic insulators, and covalent semiconductors are beset with the difficulties of having to consider the full (non-muffin-tin) crystal potential and to explicitly account for charge redistribution and hybridization processes by means of a fully self-consistent treatment. We have recently developed^{10,11} the fully self-consistent numericalbasis-set linear combination of atomic orbitals (LCAO) discrete variational method. This scheme permits the treatment of general (analytic or numerical) basis functions and crystal potentials and

the determination of fully self-consistent solutions of the LDF one-particle equation without restricting the iterative path to muffin-tin charge densities⁷⁻⁹ or to superposition models.⁵ Applications of this approach include the study of the groundstate properties of diamond,¹² boron nitride,¹³ titanium disulfide,¹⁴ cadmium sulphid, and LiAl.

The present study extends our treatment to ionic solids, for which LiF has been chosen as a prototype. We first consider the description of groundstate properties of the system, such as the band structure, charge density, x-ray scattering factors, cohesive energy, equilibrium lattice constant, and behavior under pressure, and compare the predictions of the LDF model with both experimental data and with available restricted Hartree-Fock (HF) results.¹⁵ We then consider the excitedstate properties of the system by first using the standard band approach to excitation energies (i.e., viewing them as differences in the band eigenvalues between unoccupied and occupied bands). Contrary to what has been previously suggested,¹⁶⁻¹⁸ we find that, whereas this approach

has proved to yield remarkably accurate excitation spectra for many insulators, it fails completely in the case of a heteropolar wide gap material such as LiF due to the localized nature of many of the electron-hole states in the system. Thus we are led to a generalized band model in which both the initial and the final crystal states are allowed to become localized to some extent and hence to exhibit relaxation, polarization, and electron-hole interaction effects. For this purpose, we use a defect superlattice representation $^{19-20}$ in which a locally excited species in the solid is viewed as a point-defect placed at the center of a large unit cell and the excitation energy is determined as the difference of total energies between independent self-consistent calculations (Δ SCF) of the corresponding excited- and ground-state systems. The effects introduced by final-state orbital relaxation and valence-band polarization by the hole state are found to be very large and to account for most of the discrepancies between the unperturbed band model predictions and the observed data. In addition, the model is used to calculate core and valence exciton states in the system by a direct diagonalization of the locally perturbed crystal Hamiltonian rather than by conventional effectivemass²¹ or perturbational Frenkel models.²² Good agreement is found with the experimentally observed exciton energies and binding over a large spectral region. Electron-hole interaction energies are found to be very large (2-9 eV) and to vary considerably as one moves from a deep core to a valence-state exciton. The exciton bandwidth is calculated directly from the self-consistent perturbed crystal wave functions using standard techniques and is found to be rather large (0.3 eV) for valence excitons.

II. METHOD OF CALCULATION

Since a detailed description of the method has been given^{10,11} previously, we outline here only those aspects pertinent to the present study. Our purpose is to solve the local-density one-particle eigenvalue equation for a periodic solid,

$$\left\{-\frac{1}{2}\nabla^2 + V(\rho(\vec{\mathbf{r}}))\right\}\psi_i(\vec{\mathbf{k}},\vec{\mathbf{r}}) = \epsilon_i(\vec{\mathbf{k}})\psi_i(\vec{\mathbf{k}},\vec{\mathbf{r}})$$
(1)

for band index j and Brillouin-zone (BZ) wave vector $\mathbf{\vec{k}}$. Here $V(\rho(\mathbf{\vec{r}}))$ is the crystal one-body potential given as a functional of the self-consistent crystal charge density $\rho(\mathbf{\vec{r}})$ and includes an electron-nuclear and electron-electron Coulomb term $V_{\text{Coul}}(\rho(\mathbf{\vec{r}}))$ (which includes the electron self-interaction) and a local exchange² $V_x(\rho(\mathbf{\vec{r}}))$ and correlation^{3,23} term $V_{\text{corr}}(\rho(\mathbf{\vec{r}}))$.

We first assume a population-dependent superposition model for $\rho(\vec{r})$ made up of the free-ion

(or free atom) densities $\rho_{\alpha}(\vec{r}, \{f_{n, l}^{\alpha}, Q^{\alpha}\})$ (obtained from a self-consistent numerical solution of the single-site LDF equation with the assumed ionic central field occupation numbers $\{f_{nl}^{\alpha}\}$ and net charge Q^{α}) and lattice summed to yield $\rho_{\sup}(\vec{\mathbf{r}}, \{f_{n,l}^{\alpha}, Q^{\alpha}\})$. This initial density is used to obtain an initial guess for the crystal potential $V_{sup}(\rho_{sup}(\vec{r}\,))$ in terms of $V_{Coul}(\rho_{sup}(\vec{r}\,))$ and $V_x(\rho_{\sup}(\vec{r}\,)) + V_{corr}(\rho_{\sup}(\vec{r}\,))$. The long-range part of the screened Coulomb potential is calculated by the Ewald technique.¹⁰ The crystal wave functions $\psi_i(\vec{k}, \vec{r})$ are then expanded in an LCAO form in terms of the Bloch functions $\Phi_{\mu\alpha}(\vec{k},\vec{r})$ defined by (the μ th orbital) basis functions $\chi^{\alpha}_{\mu}(\vec{\mathbf{r}})$ (on lattice site α) which are accurate numerical solutions of the single-site LDF one-particle equations for the assumed occupations and charges $\{f_{n,l}^{\alpha}, Q^{\alpha}\}$. For LiF we use the Li 1s, 2s, and 2p orbitals and the F 1s, 2s, 3s, 3p, and 3d orbitals.

The matrix elements of $V_{sup}(\rho_{sup}(\vec{r}\,))$ in the Bloch basis $\Phi_{\mu\alpha}(\vec{k},\vec{r}\,)$ are evaluated by direct three-dimensional Diophantine numerical integration²⁴ without any shape approximation to the potential and include *all* the overlap and multicenter integrals between orbitals on lattice sites separated by less than 23 a.u. The secular equations are diagonalized for a set of 10 special \vec{k} points in the irreducible BZ²⁵ and the linear LCAO expansion coefficients $C_{\mu\alpha j}(\vec{k}\,)$ are used to construct the output crystal density $\rho_{cry}(\vec{r}\,)$. Convergence tests for the radius of real-space lattice sums, the BZ sums, and the basis-set expansion have assured an overall stability of the eigenvalues to within 0.05 eV over the entire band-structure range studied.

We then start a two-stage iterative self-consistent (SC) procedure: in the first stage $\{f_{n,l}^{\alpha}, Q^{\alpha}\}$ are varied iteratively to minimize the difference $\Delta \rho(\vec{\mathbf{r}}) = \rho_{\text{cry}}(\vec{\mathbf{r}}) - \rho_{\text{sup}}(\vec{\mathbf{r}}, \{f_{n,l}^{\alpha}, Q^{\alpha}\}) \text{ in the least-}$ squares sense over the unit cell space where the basis set $\chi^{\alpha}_{\mu}(\vec{r})$ and the potential $V_{sup}(\rho_{sup}(\vec{r}))$ are optimized accordingly at each iteration (4 iterations are needed). After $\Delta \rho(\vec{r})$ has been minimized by selecting the optimum superposition model in terms of $\{f_{n,l}^{\alpha}, Q^{\alpha}\}$, we project, in the second stage of SC, the residual $\Delta \rho(\vec{\mathbf{r}})$ onto a set of symmetrized plane waves and solve the associate Poisson equation analytically in terms of the projected coefficients $\Delta \rho(\vec{K}_s)$ for a list of reciprocal lattice vectors \vec{K}_s . This reciprocal space expansion converges rapidly (about 10 stars of \vec{K}_s are needed) because the *residual* $\Delta \rho(\mathbf{\vec{r}})$ is spatially smooth. The correction to the Coulomb interelectronic potential $\Delta V(\vec{r})$ is then added to the $V_{sup}(\rho_{sup}(\vec{r}))$ obtained in the final iteration of stage 1 and this new Hamiltonian is diagonalized. The iterations in stage 2 are carried out so as to diminish the residual $\Delta \rho(\vec{K}_s)$ to a prescribed tolerance of $10^{-5}e$



FIG. 1. Self-consistent local-density potential in LiF along the [100] bond direction. The position of the edge of the valence band $\Gamma_{15,\,\nu}$ is indicated.

(5 iterations are needed).

The various components of the final SC crystal potential (along the bond [100] direction) are depicted in Fig. 1, namely, the long-range Madelungtype Coulomb part $V_{LRC}(\vec{r})$, the exchange-correlation part $V_{xc}(\mathbf{r}) = V_x(\mathbf{r}) + V_{corr}(\mathbf{r})$ and the short-range Coulomb potential $V_{\text{SRC}}(\vec{r})$ (due to direct wavefunction overlap). The potential is seen to be very shallow in the interionic region and contrary to the situation which occurs in covalent systems like diamond¹⁰ or boron nitride,¹³ the exchange-correlation part dominates the Coulomb contributions in this region. The Coulomb potential was found to be highly nonisotropic around the ionic sites (both due to the substantial penetration of the long-range Li 2s and 2p orbitals into the fluorine core and to the asymmetry of the crystal-field Madelung potential) and hence muffin-tin models²⁶⁻²⁸ as well as truncation approximations to the exchange part^{29,30} would seem inappropriate. The final crystal density $\rho_{\rm crv}(\vec{r})$ is used to calculate the total energy per unit cell by the procedure previously described.^{10,11} Again three-dimensional Diophantine integrations are needed to obtain quantities such as $\int \rho_{\rm crv}(\vec{\mathbf{r}}) V(\rho(\vec{\mathbf{r}})) d\vec{\mathbf{r}}$ which converge much slower than those necessary in the band-structure study (although the convergence rate is better than in

analogous molecular studies⁶); a large number of Diophantine integration points (2000 per Li and 3000-4000 per F) together with an improved sampling point mapping scheme are needed to obtain an accuracy of 0.5-0.3 eV in the total energy. All our calculated binding energies are given later with this value as a possible error.

III. RESULTS FOR THE GROUND STATE

A. Band structure

The self-consistent band structure of LiF obtained in the exchange model with $\alpha = \frac{2}{3}$ and 1 is shown in Fig. 2. The positions of the free-ion and free-atom eigenvalues corresponding to these two models are indicated by the horizontal lines on the right-hand side with the former shifted by the Madelung potential (-12.45 and +12.45 eV for F and Li⁺, respectively). The main difference between them is a downward shift of the valence bands by about 3 eV in the α = 1 case accompanied by a smaller shift in the conduction bands; this results in a smaller band gap in the $\alpha = \frac{2}{3}$ case (9.8 eV) relative to the $\alpha = 1$ result (10.5 eV). While the occupied fluorine 2s band (containing some admixture with Li 2s) and the valence 2p-like band appear very close in position to both the 2s, 2ppoint-ion corrected free-ion and free-atom eigenvalues, the conduction band is very wide and does not show any close correspondence to the position of the virtual free-ion Li 2s and 2p orbital energies. At lower energies (not shown in Fig. 2) are the Li 1s core band (-58.4 eV, $\alpha = 1$) and the fluorine 1s core band ($-680.9 \text{ eV}, \alpha = 1$), both essentially unshifted relative to the corresponding pointion corrected ionic eigenvalues.

Since $several^{16, 17, 29, 30}$ of the many published local density band structures²⁶⁻³² of LiF were carried to full self-consistency using the complete potential, a meaningful comparison with our results can be made. Drost and Fry²⁹ and Brener³⁰ used an atomic Gaussian set (i.e., 10 Bloch basis functions) and a muffin-tin-like treatment of the iterated exchange potential; Chaney et al.17 and Menzel et al.16 employed an extended Gaussian set (54 basis functions) and a real-space-fitting procedure to evaluate the multicenter Coulomb and exchange integrals. All four calculations^{16, 17, 29, 30} were done in the $\alpha = 1$ exchange model and used as a starting guess to the crystal density a superposition of Hartree-Fock atomic densities with fixed Gaussian exponents taken over largely from atomic Hartree-Fock calculations.³³ By contrast, we employ directly nonlinearly optimized local density (numerical) ionic basis functions as our initial guess for constructing the crystal density.^{34,35} Although differences between these choices might be im-



FIG. 2. Self-consistent band structure of LiF in the $\alpha = \frac{2}{3}$ exchange model (left) and in the $\alpha = 1$ exchange model (right). The horizontal bars on the right-hand side of each figure indicate the corresponding point-ion corrected free-ion eigenvalues of F⁻ and Li⁺ and the free-atom eigenvalues of F⁰ and Li⁰.

material from the variational point of view (provided reasonable basis-set convergence and selfconsistency is maintained), from the practical point of view, our choice seems to offer higher efficiency due to its closer consistency with the local density crystal Hamiltonian representation considered.³⁶ On the other hand, muffin-tin-like approximations to the iterated exchange^{29,30} might be more of a problem due to the large amplitude of the exchange potential in the interionic region in this material relative to the electrostatic contributions (Fig. 1).

Table I compares our band eigenvalues at some high-symmetry points in the BZ using both a minimal and an extended local density (ionic) numerical basis set with those of Menzel *et al*,¹⁶ the correct ed^{37} results of Drost and Fry.²⁹ (The virtual numerical orbitals for F⁻ were computed from an F⁻ ion placed in a localizing potential well with a

13-a.u. radius. This serves both to produce the required bound states and to localize the otherwise diffuse 3s to 3d orbitals.) All calculations presented in the table were done with $\alpha = 1$ and a lattice constant of 4.017 Å. The agreement between the 54 Gaussian calculation¹⁶ and our minimal numerical basis set (10 functions) is good over a region of about 25 eV (to about 0.1 eV in the valence bands and 0.3 eV in the conduction bands, except for the highest $\Gamma_{15,c}$ point). A substantial increase in our basis set (column 4 in Table I) produces only negligible changes in the valence bands relative to the minimal numerical set; however, the high d-like conduction bands are now more severely affected (e.g., a 0.6-eV shift in $\Gamma_{15,c}$). Hence we conclude that a minimal local density ionic basis set is sufficient to produce an accuracy of about 0.15 eV for eigenvalues in the range of $1-1\frac{1}{2}$ Ry above the valence band. Similar conclusions were

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Level	54 Gaussians ^a	LCAO Minimal numerical ^b	LCAO Extended set ^c	LCAO Gauss ^d (10 G)
Γ _{15,ν}	0.0	0.0	0.0	0.0
$X_{4,v}$	-0.090	-0.086	-0.085	-0.046
$L_{2,v}$	-0.077	-0.075	-0.075	-0.044
$X_{5,v}$	-0.030	-0.028	-0.029	-0.015
$L_{3,v}$	-0.007	-0.007	-0.007	-0.003
$\Gamma_{1,c}$	0.389	0.393	0.386	0.578
$L_{1,c}$	0.466	0.473	0.470	0.699
$X_{4,c}$	0.587	0.599	0.592	0.732
$L_{2,c}$	0.658	0.668	0.666	0.822
$X_{1,c}$	0.701	0.713	0.710	1.020
$L_{3,c}$	0.812	0.808	0.801	0.911
$X_{5,c}$	0.833	0.824	0.812	0.898
$\Gamma_{15,c}$	0.929	0.974	0.953	1.016
E_g (eV)	10.58	10.70	10.50	15.71
VBW (eV)	2.45	2.34	2.31	1.25

TABLE I. Self-consistent band structure of LiF in the α =1 exchange model. Results for the eigenvalues are given in atomic units; the band gap (E_g) and valence-band width (VBW) are given in eV.

^a Reference 16.

^b Present results with a numerical set consisting of $F^{-1}s, 2s, 2p$ and $Li^{+1}s, 2s, 2p$ local-density orbitals (10 basis function).

^c Present results with addition of $F^{-}3s, 3p$ (23 basis functions).

^d References 29 and 37.

drawn in our previous studies of diamond $^{\rm 10}$ and boron nitride. $^{\rm 13}$

The results of Drost and Fry²⁹ (column 5 in Table I) are in very poor agreement with those of the present study and with those of Menzel et al.¹⁶ The order of the $L_{3,c}$ and $X_{5,c}$ levels is reversed, the $X_{1,c}$ level is completely misplaced, and quantitative differences occur (as much as 1.1 eV in the valence bands and 7 eV in the lower conduction bands). We do not think these differences are due solely to the small size of their basis set (similarly small basis sets have been shown¹⁷ to produce smaller differences) but rather to their treatment of the exchange potential.³⁸ We find similar differences between our results and the muffin-tin calculations.^{27,28} Further, non-self-consistent calculations^{31, 32} show large (2-3 eV) deviations even in the low edge of the conduction band (including a false minimum at $L_{1,c}$ ³².

To investigate the separate effects of the exchange and the correlation potentials on the band structure we have performed two independent $\alpha = \frac{2}{3}$ self-consistent calculations, one with the correlation functional²³ included in the crystal potential (exchange and correlation model) and one without it (exchange model). The results for the valence bands of LiF are shown in Fig. 3. The main effect of the correlation functional is to shift the bands downward almost rigidly by about 0.8 eV, but with a nonrigid (\mathbf{k} -dependent) effect of about 0.1 eV. The band gap is increased by about 0.1 eV and the valence band width is broadened by a similar amount. While these changes are hardly material as far as the joint density of states is concerned, they are important for both the total energy (and binding energy) calculations as well as for the determination of the ionization threshold in the solid.

Painter³¹ demonstrated that scaling the exchange parameter α between $\frac{2}{3}$ and 1 had a significant effect on the band structure at the non-SC limit (e.g., the band gap increases from 10.3 to about 16 eV). This was explained in terms of the lower sensitivity of the Li(2s)-like bottom of the conduction band $(\Gamma_{1,c})$ to exchange scaling relative to the F(2p)-like top of the valence band $(\Gamma_{15, v})$ which shows substantial charge localization on the fluorine sublattice. Our results (cf., Fig. 2) show that in the SC limit, the differences between the $\alpha = \frac{2}{3}$ and $\alpha = 1$ are much smaller (e.g., an energy gap of 9.8 eV versus 10.5 eV for $\alpha = \frac{2}{3}$ and 1, respectively). This diminished difference is brought about by the removal of electronic density from the interstitial region to the ionic sites during the SC iterations, thereby increasing the charge localization on the Li ions and hence tending to equalize the sensitivity of the $\Gamma_{1,c}$ and $\Gamma_{15,v}$ states to exchange scaling. In addition, the Li 2s and 2p basis



FIG. 3. Structure of the valence bands of LiF in the exchange model and in the exchange and correlation model. Both calculations employ an exchange coefficient of $\frac{2}{3}$ and an optimized minimal numerical basis set (see text).

orbitals become spatially more contracted during SC iterations due to the nonlinear orbital optimization procedure used, allowing these formerly virtual orbitals to become fractionally occupied. Both these linear and nonlinear mechanisms act to equalize the exchange scaling sensitivity of the band edges and show up only in a fully self-consistent treatment.

B. Charge analysis of the ground-state bands

A charge analysis^{39,40} of the crystal wave functions was performed in order to obtain the orbital character of the occupied valence bands in LiF. A simple identification of the square of the linear variation coefficient $|C_{\mu\alpha j}(\vec{k})|^2$ with contribution of the μ th ionic orbital on sublattice α to the charge associated with the band state $|\vec{k},j
angle$ would be highly unrealistic due to the pronounced nonorthogonality of the Bloch basis $\Phi_{\mu\alpha}(\vec{k},\vec{r})$ (in particular, the Li 2s and 2p orbitals are quite diffuse with sizable amplitudes on the F sites). Instead, we adopt the Löwdin charge analysis⁴⁰ used in molecular structure calculations, orthogonalize the Bloch basis set using a symmetric transformation,⁴⁰ and then associate the square of the coefficient $|\tilde{C}_{\mu\alpha i}(\vec{k})|^2$ in the orthogonal representation with the $\mu \alpha$ orbital charge due to state $|\vec{k}, j\rangle$. Summing these partial charges over all the occupied bands j, we obtain the contribution $q_{\mu\alpha}(\vec{k})$ of orbital μ on site α



FIG. 4. BZ dispersion of the orbital charges $q_{\mu\alpha}(\vec{k})$ in the ground state of LiF. The orbital charges corresponding to the free Li⁺ and F⁻ ions are shown by the horizon-tal lines at the right-hand side.

to the charge at point \vec{k} in BZ. The BZ dispersion of $q_{\mu\alpha}(\vec{k})$ is displayed in Fig. 4; integration of $q_{\mu\alpha}(\vec{k})$ over the BZ yields the total ground-state charge due to orbital μ on site α .

Figure 4 shows that, except for the F⁻1s and Li⁺ 1s core charges, all other orbital charges exhibit pronounced variations across the BZ; the crystal electronic configuration at Γ is $Li^{+0.38}[1s^{1.910}2s^{0.665}2p^{0.045}]$ and $F^{-0.38}[1s^{2.00}2p^{1.42}2p^{5.96}]$ in terms of the ionic numerical orbitals while higher charge polarization occurs at the X point, characterized by the configuration $\text{Li}^{+0.45}$ $[1s^{1.97}2s^{0.06}2p^{0.52}]$ and $F^{-0.45}[1s^{2.00}2s^{1.97}2p^{5.43}]$. Appreciable mixing of Li 2s character occurs near Γ while along the Δ -*X*-*W*-*K* and *L*-*W* directions there is a non-negligible Li 2p character with only minor Li 2smixing. The fluorine 2s and 2p charges have lower values than in the idealized free-ion configuration (2 and 6 electrons, respectively) and likewise show considerable BZ dispersion. Hence, although solid LiF is a closed-shell system in its ground state, its common description in terms of closed-shell ions⁴¹ is inappropriate in the context of a realistic LCAO model which includes all the nonorthogonality terms. Similarly, it appears that the common description of a strongly ionic material such as LiF in terms of tightly bound short-range cation and anion orbitals^{42,43} is oversimplified; as a matter of fact, the non-negligable charge density in the interionic regions in the crystal is largely donated by the rather diffuse (formerly virtual) cation orbitals which are unoccupied in the free ions and

which act to stabilize the crystal electrostatically by penetrating the attractive core regions near the anions. Previous cohesive energy studies of alkali halides⁴²⁻⁴⁵ have largely used Löwdin orthogonalized *free ion* orbitals to approximate the single-site Wannier functions in the solid. Our results for LiF indicate that a better choice is to use similarly orthogonalized single-site orbitals but with fractional occupations corresponding to the variationally determined *crystal* orbitals which are distinctly different from the closed-shell ionic orbitals (Fig. 4).

The population analysis of the kind shown in Fig. 4 can be used to improve the variational quality of a minimal basis set in crystalline LCAO calculations; by performing a BZ average over each of the orbital charges $q_{\mu\alpha}(\vec{k})$, one obtains the effective electronic configuration of each ion in the solid in its ground state. These can be used to solve the free-ion local density equations to obtain improved basis functions for the solid. In this manner, nonlinear optimization of the basis set is obtained. The results of such a calculation showed that a minimal basis set corresponding to the exact local density free-ion wave functions of the $Li^{+0.43}[1s^{1.97}2s^{0.16}2p^{0.44}]$ and $F^{-0.43}[1s^{2.0}2s^{1.72}2p^{5.71}]$ ions produced a band structure that agrees to about 0.05 eV with that obtained by the unoptimized extended basis set (Table I) for energies lower than ~ 1.3 Ry above the valence band edge. This choice of basis set, when used for generating a superposition crystal density and the resulting band structure, also minimizes the difference between the output crystal density and the superposition density and hence serves as an optimum minimal set. The major change in the wave functions of the optimized configuration is a contraction of the fluorine 2p shell. This basis set is very economical to use and was employed in further calculations, except for the total energy calculation which required a larger set.

C. Charge density and x-ray scattering factors

The orbital population analysis tells us only about the overall *mixing* of each orbital species in the occupied manifold, but does not indicate the degree to which such orbitals contribute to *bonding* (i.e., their spatial behavior in the core and interionic region). The orbital density $\rho_j(\vec{k}, \vec{r}) = \psi_j^*(\vec{k}, \vec{r})\psi_j(\vec{k}, \vec{r})$ for several of the occupied high-symmetry points is shown in Fig. 5. The bottom of the F⁻(2s)-derived valence band, at $\Gamma_{1,v}$, is shown to have some hybridization with the Li 2s wave function (cf., Fig. 4). The appreciable long tail of the Li 2s orbital causes its admixture into the occupied bands to create a nonvanishing density in the bond region



FIG. 5. Orbital charge density, $\mu_j(\vec{k},\vec{r}) = \psi_j^*(\vec{k},\vec{r})$ $\times \psi_j(\vec{k},\vec{r})$, for several high-symmetry points in the BZ of LiF plotted along the [100] bond direction.

and to enhance the charge buildup at the F site. Somewhat higher in energy in the $F^{-}(2s)$ -derived band, we find the $L_{1,v}$ level which is made up of $F^{-}2s$ orbitals hybridized with some Li 2p orbitals (viz., the nodal character at the Li site). Higher in energy we find at the $X_{5,v}$ point in the $F^{-}(2p)$ -derived valence band an F(2p)-Li(2p) hybrid (cf., Fig. 4); as one moves to the zone center ($\Gamma_{15,v}$), a predominantly F 2p state is formed.

Figure 6 shows the total ground-state charge density calculated in the exchange model (1) and in the exchange and correlation model (2), along the [100] direction in the unit cell. The position of their minima is given in Table II, and compared with the relevant experimental determination.^{46,47} These quantities are given here as a percentage of the lattice constant (i.e., twice the nearest-neighbor distance), as is commonly done in the literature. Unlike the older measurements of Krug et al.⁴⁶ (in which dispersion corrections were not applied and rather high fluorine Debye-Waller factors used) which show a substantially larger Li radius, more recent structure factor measurements⁴⁸⁻⁵⁰ seem to agree better with the data of Merisalo and Inkinen47 which exhibit systematically shorter metal radii. Our results agree better with the latter data and indicate that the effect of correlation is to expand the electropositive Li site at the expense of contracting the electronegative F. In this context it is interesting to note that Pauling's ionic radii (0.6 Å for Li⁺ and 1.36 Å for



FIG. 6. Total ground-state charge density calculated in (1) the exchange and correlation model, and (2) the exchange model along the [100] direction in the unit cells. The arrows point to the positions of minimum density in the corresponding models.

F⁻) predict a much larger disproportion between the size of the lattice ions $(15.3\% \text{ and } 34.7\% \text{ for Li}^*$ and F⁻, respectively) than do both the observed and the calculated values in the crystal.

The precise value of the minimum charge density in the unit cell is difficult to evaluate accurately from the experimental data since small changes in the temperature parameters and structure factors introduce significant changes into this small quantity. The measurements of Krug *et al.*⁴⁶ indicate a minimum density of 0.19 $e/Å^2$ (0.028 $e/a.u.^3$) while that of Merisalo and Inkinen⁴⁷ show a minimum of approximately 0.15 $e/Å^3$ (0.022 $e/a.u.^3$). While our calculation shows a minimal density of 0.155 $e/Å^3$ (0.023 $e/a.u.^3$) in good agreement with both measurements, the large uncertainties in the

TABLE II. The distances from Li and F sites, at which the charge density reaches a minimum, expressed as a percentage of the lattice constant a=4.018 52 Å.

	Exchange and correlation model	Exchange model	Exp ^a	Exp ^b
R _{Li} R _F	19.2 30.8	$\begin{array}{c} 17.5\\32.5\end{array}$	19.4 30.6	$\begin{array}{c} 22.9\\ 27.1 \end{array}$

^a Reference 47.

^b Reference 46.

observed values may make this agreement fortuitous. It is interesting to note that Hartree-Fock *molecular* calculations⁵¹ predict a much higher minima along the Li-F bond, namely, 0.675 $e/Å^3$ (0.1 $e/a.u.^3$).

Table III shows the total (numerically integrated) electronic charge enclosed in spheres of varying sizes around the Li and F sites whose radii are chosen to form touching spheres. The results are in remarkably good agreement with the measured data of Merisalo and Inkinen.⁴⁷ We find in our exchange and correlation model that the radius at which the Li sphere enclosed exactly 2.0 electrons is 0.69 Å (17.1% of the lattice parameter), which is only slightly smaller than the position of the minimum in the charge density (17.5% given in Table II), at which the Li sphere contains 2.05 electrons.

Table IV compares our calculated x-ray structure factors with those calculated in the Hartree-Fock model^{15,52} and with the observed data⁴⁷ with the temperature factors removed.⁵³ The x-ray structure factors are calculated in two different approximations: (i) In a spherical atomic model which assumes that the crystal charge density can be represented as a lattice sum of (overlapping) spherical ion densities, one finds that the crystal structure factors are given simply by $F_{h,k,l}^{+}$ = 4 [$f_{h,k,l}^X + f_{h,k,l}^M$] for the even (h,k,l) reflections and by $F_{h,k,l} = 4[f_{h,k,l}^X - f_{h,k,l}^M]$ for the odd reflections, where $f_{h,k,l}^X$ and $f_{h,k,l}^M$ stand for the spherical anion and cation scattering factors, respectively. The crystal $F_{h,k,l}^{\pm}$ values calculated in this way using free-ion Hartree-Fock and local exchange wave functions are given in columns 2-4in Table IV. (ii) In a crystal model, the scattering factors are computed directly from a three-dimen-

TABLE III. Calculated (exchange and correlation model) and observed number of electrons g(R) in spheres of radius R around the Li and F sites.

	Calculated $g(R)$ (e)	Measured (Ref. 47) $g(R)$ (e)
$R_{\rm Li}$ (Å):		
0.93	2.25	2.22
0.83	2.16	2.12
0.78	2.11	2.07
0.73	2.05	2.03
0.63	1.94	1.91
$R_{\rm F}$ (Å):		
1.08	9.01	9.06
1.18	9.30	9.35
1.23	9.47	9.48
1.28	9.61	9.60
1.38	9.68	9.72

511

hkl	Atomic (spherical) HF ^a	Atomic (spherical) LDF; $\alpha = \frac{2}{3}$	Atomic (spherical) LDF; $\alpha = 1$	Atomic nonspherical HF ^a	Crystal HF ^b	Crystal LDF $\alpha = \frac{2}{3}$	Exp ^c
200	7.62	7.49	7.72	7.72	7.70	7.79	7.72
220	5.71	5.65	5,95	5.78	5.72	5.69	5.70
222	4.61	4.58	4.86	4.66	4.60	4.66	4.60
400	3.90	3.88	4.12	3.94	3.90	4.03	3.99
420	3.41	3.40	3.60	3.44	3.40	3.48	3.45
422	3.05	3.05	3.22	3.08	3.04	3.11	3.07
440	2.58	2.57	2.63	2.60	2.57	2.57	2.57
600	2.41	2.40	2.45	2.43	2.41	2.40	• • •
442	2.41	2.40	2.45	2.43	2.41	2.40	2.40
111	4.89	4.77	4.90	4.96	4.98	4.88	4.84
311	2.36	2.38	2.55	2.38	2.36	2.39	2.36
331	1.65	1.69	1.76	1.65	1.63	1.71	1.65
333	1.38	1.42	1.44	1.37	1.36	1.43	1.37

1.37

1.37

1.44

TABLE IV. Calculated and observed x-rays scattering factors for LiF.

^a Reference 52.

^b Reference 15.

1.38

1.42

^c Reference 47.

sional Fourier transform of the BZ averaged crystal density, without assuming the separability of the latter to a lattice sum of free-ion-like densities. Columns 6 and 7 in Table IV compare the crystalline Hartree-Fock results of Euwema et al.¹⁵ with those of the present LDF study. Column 5 gives the structure factors calculated by Aikala and Mansikka⁵² from free-ion Hartree-Fock wave functions but with inclusion of nonorthogonality corrections due to *wave-function* overlap up to first- and second-nearest-neighbor for the Li⁺ and the F⁻ sublattices, respectively. (A direct incorporation of such an interionic overlap generates nonspherical components of the charge density around each site and forms a better approximation to the crystal scattering factor.)

Several conclusions can be drawn from this comparison: (i) The spherical free-ion HF model yields lower $F_{h, k, l}$ values than the $\alpha = 1$ LDF model, but higher values than those obtained with the $\alpha = \frac{2}{3}$ LDF model. The HF charge density is hence more spatially diffuse than that yielded by the $\alpha = 1$ results but slightly more contracted than that predicted by the $\alpha = \frac{2}{3}$ calculation. The exchange and correlation model with $\alpha = \frac{2}{3}$ produced values that are slightly larger than those produced by the $\alpha = \frac{2}{3}$ exchange-only model. (ii) Nonspherical corrections⁵² to the free-ion HF model produce a more localized charge density (i.e., have the effect of approaching the LDF spherical results with α greater than $\frac{2}{3}$). (iii) The crystalline HF and LDF results show a general increase in the structure factors relative to the corresponding spherical free-ion results which is much larger in the LDF

model than in the HF model. The increase in the HF crystalline structure factors relative to the spherical free-ion limit seems insufficient to account for the experimental crystal data and is significantly lower than that yielded by the nonspherical free-ion HF model. This might reflect both numerical inaccuracies in the crystal HF model, which is significantly more complex than the nonspherical free-ion model, and the superiority of the Slater basis set representation $^{\rm 52}\ensuremath{\,\text{used}}$ in the latter as compared with a Gaussian set used in the crystalline HF model. The overall agreement of both the HF and the LDF crystal results with experiment is good, with the HF systematically lower and the LDF systematically higher than the observed results.

1.42

1.37

D. Behavior under pressure

Figure 7 shows the variation with lattice constant of some high-symmetry energy levels in the conduction bands (labeled A), $F^{-}(2p)$ -derived valence bands (labeled B), and the F(2s)-derived bands (labeled C). Also shown are the free-ion eigenvalues (denoted $\epsilon^{0}_{\alpha\mu}$) shifted by the Madelung potential at the ionic site (V_M) for each of the 8 unit cell parameters at which calculations were done between 3.90 and 4.17 Å. The first striking feature of these results is the linearity of the curves. It is seen that the variation of the valence band (Band C) energies with lattice constant follows essentially that of the point-ion potential at the fluorine site (dashed lines in regions B and C). This behavior is expected when only small admixtures of



FIG. 7. Lattice-constant dependence of some highsymmetry points in the band structure of LiF. Bands belonging to conduction states are denoted by A, $F^{-}(2p)$ derived bands are labeled by B and $F^{-}(2s)$ -derived bands are denoted by C; dashed lines indicate the variation of the Madelung corrected $(\pm V_{M})$ free-ion eigenvalues $(\epsilon_{\alpha\mu}^{0}$ for $\alpha = F^{-}$, Li⁺ and $\mu = 2s$, 2p) in the local-density model. E_{g} denotes the band gap.

the positive-site wave functions are permitted and the repulsive non-Madelung forces (i.e., shortrange Coulomb and exchange) are relatively weak. On the other hand, the conduction bands (A) show a more complex behavior with lattice constant variation: the bottom of these bands ($\Gamma_{1,c}$), being almost of pure Li character, follows essentially the $\epsilon_{\text{Li},2s}^0 + V_M$ curve; the next higher states (e.g., $W_{3,c}, X_{4,c}$) contain some fluorine character and hence show only weak lattice constant dependence due to extensive cancellation between the positive site and negative site point-ion contributions. The high-energy conduction states ($X_{5,c}, \Gamma_{15,c}$) increase in energy with decreasing lattice parameter more rapidly than does the positive ion Madelung potential due to their antibonding character [i.e., their energy is proportional to $(1 - 2S_{\alpha\beta})^{-1}$, where $S_{\alpha\beta}$ is the lattice-parameter-dependent overlap integral between nearest-neighbor lithium sites and hence small changes in the lattice parameter produce large changes in the eigenvalues]. The band gap E_{e} at Γ and the valence band width increase monotonically with decreasing lattice constant, the former being affected much more markedly (about 1.5 eV over the range studied) than the latter for the reasons discussed above. Thus it would seem that the pressure dependence of the optical transition energies in this material would follow a rather complex behavior due to the interplay between electrostatic and initial- and final-state hybridization effects. We are unaware at present of any relevant experimental data with which to test these predictions.

E. Cohesive energy and equilibrium lattice constant

To further study the performance of the local density formalism on ground-state properties of ionic solids, we have calculated the binding energy and equilibrium lattice constant of LiF. The total crystal energy of LiF has been calculated by the method previously described.^{10,11} The charge density and eigenvalues were sampled at 10 wave vectors in the irreducible section of the BZ. This sampling mesh is more than adequate in view of the narrow valence bands of LiF (Fig. 2) and the relatively low dispersion of the crystal orbital density $\rho(\vec{k}, \vec{r})$. About 5000–6000 Diophantine integration points were sufficient to obtain a convergence of 0.03%-0.016% in the total energy (the cohesive energy is about 0.4% of the total energy per cell). Although higher numerical accuracy can be obtained by increasing the number of integration points, it was felt not to be warranted at this stage because of the large combined effect of all the other approximations [truncation of higher-order terms in the expression for the expansion of the total exchange and correlation energy,¹⁻³ basisset effects, and replacement of the integral over the BZ by a discrete sum for calculating $\rho_{erv}(\vec{r})$]. The total energies of the free ions were calculated by standard procedures¹¹ (accurate to within 0.001%). The total energy of the crystal was calculated at 8 values of the lattice parameter and a smooth curve was fitted to find its minimum. The cohesive energy is defined here relative to the energy of the ionic dissociation products.

We have used two basis sets for the calculation: the optimized minimal numerical set (denoted I, see Sec. III B), and the extended basis set (denoted II) and including F⁻ 1s, 2s, 2p, 3s, 3p, and 3d and Li^{*} 1s, 2s, and 2p numerical orbitals. Set I yields a binding energy E_B of $9.3 \pm 0.5 \text{ eV/pair}$ at the *observed*⁵⁴ lattice constant a = 4.018 Å and is close to the value of $9.5 \pm 0.5 \text{ eV/pair}$ obtained by the larger set II. This small difference is perhaps not entirely surprising since the major contribution to the cohesive energy arises from the basis-set-independent long-range electrostatic field (12.4 eV) while the repulsive (basis-set-dependent) contribution forms only about 20% of the cohesive energy. The observed³⁴ E_B of LiF, corrected for the zero-point energy (using a Debye formula) is 10.6 eV/pair.

16

The situation is quite different regarding the *calculated* equilibrium lattice constant a_{eq} : while basis set I predicts $a_{eq} = 4.18 \pm 0.03$ Å which is substantially larger than the observed value of 4.018 $\pm\,0.03$ Å, 54 the extended set II predicts an improved value of 4.09 ± 0.03 Å with a cohesive energy of 9.8 ± 0.5 eV/pair at this equilibrium value. (The error bars given to the computed lattice constants refer to the fitting and interpolation of the calculated total energies at the different lattice constants.) Hence, while even a medium quality basis set is capable of predicting reasonable values of the cohesive energy of the of the system, a much improved set is needed to reproduce accurately the equilibrium lattice constant in the system. The local density model predicts an a_{eq} that is 1.8% too large and an E_B that is 7.5% too small (similar trends were observed in our local density calculations for diamond¹⁰ and boron nitride¹³). It is expected that inclusion of second-order dispersion forces not present in our model (i.e., that part of the interaction that exists even at zero overlap between the subsystems and is contributed by intermediate virtual states) would act to reduce a_{eq} somewhat and increase E_{B} and so yield closer agreement with experiment.

Our determination of the cohesive energy and zero-pressure lattice constant of LiF can be compared with several nonempirical studies based on the Hartree-Fock model. We note two basic approaches to the problem:

(i) The model of Löwdin,⁴⁴ which is an elaboration of the pioneering work of Hylleraas⁵⁵ and Landshoff,⁵⁶ treats the problem by replacing the canonical crystal density with a lattice sum of single-site densities and evaluates directly the (nonlocal) exchange and Coulomb contribution of each site to the binding energy. Although such a partitioning of the density can (in principle) be determined variationally from the crystal Hamiltonian (e.g., by solving the problem in the Wannier representation), in practice, an orthogonalized noninteracting *free-ion* (Hartree or Hartree-Fock) basis set was used to simulate such a single-site density. This choice is not unique and its adequacy depends entirely on the degree to which the chosen ground-state orthogonalized free-ion orbitals resemble the crystal wave functions (cf. Fig. 4). This method, when applied within the nearestneighbor approximation and with HF orbitals, yields⁴⁴ $a_{eq} = 4.1$ Å and $E_B = 10.4$ eV/pair. Later experience has shown^{52, 57} that the agreement with experiment becomes considerably poorer when second-neighbor interactions are included. Subsequent modifications of the method have attempted to introduce some radial scaling of the free-ion orbitals so as to better mimic the somewhat contracted anionic crystal orbitals⁴² (yielding $a_{eq} = 4.03$ Å and $E_{B} = 10.5 \text{ eV/pair}$) or to introduce more variational parameters in an analytic model for the anion p orbital (yielding $a_{eq} = 4.0$ Å and $E_{B} = 10.4$ eV/pair).43

(ii) The approach adopted by Euwema *et al.*¹⁵ involves a direct linear variational solution of the crystalline HF Hamiltonian and the determination of the total energy from the BZ integrated charge density. Using a Gaussian s and p basis set, this yields $a_{eq} = 3.972$ Å and $E_B = 11.2$ eV/pair. Although in good agreement with experiment, it is somewhat surprising that this approach leads to shorter bonds and higher binding than both the experimental data and the HF calculations in the modified Löwdin model.^{42-43,57} Table IV suggests that further localization in the HF crystal orbital is needed to improve agreement with the observed x-ray scattering factors; this, together with the inclusion of dispersion forces (not included in the HF model). will tend to further shorten the bond length and to increase the binding energy. A similar trend can be observed in the HF calculations on diamond.58

IV. EXCITED STATES OF LIF

A. Experimental data and band-model results

Since a ground-state one-electron band model (cf., Fig. 2) can at best account for Bloch-type interband transitions but not for exciton states that are stabilized by a localized-type electron-hole interaction, we first review the experimental data on the LiF electronic spectra in order to identify those excitations that are in principle describable by a band model. The excitation spectra of LiF can be divided into four broad spectral regions (with possible overlap between them): the F⁻ 1s region (~ 690-720 eV), the Li⁺ 1s region (~ 55-75 eV), the F⁻ 2s region (~ 30-60 eV), and the fundamental valence to conduction region (10-25 eV).

(i) The measured $F^{-1}s$ ionization energy in the solid is 693.2 eV.⁵⁹ The position of this band relative to the bottom of the conduction band is proba-

bly very close to this value due to the low electron affinity of the system.⁶⁰⁻⁶² No exciton series has so far been identified for this transition. Similarly, the excitations of this level into the conduction states [expected to start at about 708 eV since the lowest fluorinelike unoccupied virtual states (e.g., F 3s, 3d) appear (Fig. 2) at about 13-15 eV above the bottom of the conduction band] have not been measured. (ii) The Li⁺ 1s absorption spectra have been measured by several authors.⁶³⁻⁶⁸ To determine which of the observed features are excitonic and which are interband transition, one first considers the Li⁺ 1s ionization limit and its position relative to the conduction band edge. Electron spectroscopy for chemical analysis (ESCA) measurements⁵⁹ reveal an ionization energy of about 64 eV while the Li⁺ 1s to conduction separation can be deduced from the x-ray photoemission (XPS)⁶⁹ and yield spectroscopy⁷⁰ determination of the Li⁺ 1s to valence edge ($\Gamma_{15,v}$) separation (50.77 eV,⁶⁹ and 50.2 eV) and the optical determination of the valence to conduction $(\Gamma_{15, v} - \Gamma_{1, c})$ gap (14.2 ± 0.2) eV).^{71,72} This yields a value of 64.4 ± 0.8 eV for the Li^{+} 1s to conduction edge spacing (and a small electron affinity) and hence the optical transitions below this energy are due to bound excitons below the conduction threshold. In this region the optical spectra reveal a weak shoulder A' at 60.8-60.1 eV,^{64, 73, 74} with a strong peak A at 61.9 eV,^{64, 67} followed by a pronounced minimum at about 63.8 eV^{64, 67, 73} corresponding to the convergence limit of the exciton series. Above this threshold one observes the shoulders B and C at 65.1 and 68.4 eV, respectively, and a broad structure D at 70.1 $eV.^{64,73}$ Brown *et al.*¹⁸ have suggested, on the basis of a restricted HF band calculation, that peak A can be explained as an interband transition subject to long-range correlation corrections. Similarly, a local density band model of Mentzel et al.¹⁶ (with $\alpha = 1$) showed a pronounced peak in the joint density of states at about 62 eV. This was used to interpret peak A as being due to interband transitions and not to an exciton. From the above analysis of the experimental data,^{75,76} it is clear that both suggestions are incorrect in that unperturbed band models cannot account for exciton states.

The electron-energy loss spectra in the Li 1s region⁷⁷⁻⁷⁹ shows the excitons A' and A to be blue shifted at ~ 62 and 63 eV, respectively, in agreement with the longitudinal exciton energy loss shift model of Miyakawa.⁸⁰ Emission studies of Maiste *et al.*⁷⁴ and Gudat *et al.*⁷⁰ have revealed an emission band centered at 60.6 eV originating from a radiative decay of the A' and A excitons. They have tentatively identified peak A' as being due to a forbidden Li^{*} 1s-2s exciton [free-ion excitation] energy, 60.9 eV (Ref. 81)] and peak A as a Li^{*} 1s-2p allowed exciton (free-ion excitation energy 62.2 eV⁸¹). Similar studies on small-radius excitons in rare-gas solids⁸² have likewise indicated a small (0.1-0.2 eV) shift of the free-atom transition energy in the solid. The emission study of Arakawa *et al.*⁸³ has confirmed that only one emission peak (at 61 eV) exists between the top of the valence band ($50.5 \pm 0.3 \text{ eV}$) and the bottom of the conduction band ($50.5 \pm 14.2 = 64.7 \text{ eV}$) suggesting that both excitons A' and A emit from a common source. Thus it seems clear from the foregoing analysis that a band model which omits localized electron-hole interactions, can at best attempt to explain the interband peaks B, C, and D.

The interpretation of the optical transitions at 50-60 eV is a subject of substantial controversy: Milgram and Givens⁶³ did not observe any absorption structure in this region, while Sonntag⁶⁷ found a weak absorption peak at about 53 eV. The photoelectric yield studies of Gudat et al.⁷⁰ showed a weak structure in the 54-60 eV region with a small peak at 58.3 eV. Several theoretical stud $ies^{16, 75, 76, 84-87}$ have suggested that the Li⁺ 1s-2s forbidden exciton may lie at energies as low as 52 eV. It is, however, unclear whether the weak structure observed in this region is due, instead, to the tails of the F⁻2s spectra.^{67,70} Recent inelastic electron scattering experiments of Fields et al.⁸⁸ have convincingly demonstrated (by varying the transferred momentum q) that no forbidden transitions occur in the 52-60 eV region while the 61-eV peak (A') showed pronounced q dependence and was hence identified as a forbidden exciton. The assignment of ~52-eV structure as a $Li^+ 1s-2s$ transition would imply a ~ 9 eV solid-state shift relative to the free ion $Li^+ 1s-2s$ transition which is much larger than that found⁸⁵⁻⁸⁷ for the Li⁺ 1s-2pexciton (~ 0.3 eV). Clearly, a detailed theoretical study is needed to identify the origin of the observed transitions in this spectral range.

(iii) Experimental data on the F 2s excitations are very limited; ESCA studies⁵⁹ place the $F^{-}2s$ ionization potential (denoted as line X) at about 37.6 eV (using a work function of 7.07 eV). This is not too far from the free-ion $F^- 2s$ ionization energy shifted by the Madelung potential at the F⁻ site, 36.8 eV. The separation between the $F^- 2s$ level and the valence band edge has been measured by $ESCA^{59}$ (23.2 eV), XPS [24.9 eV (Ref. 69)], and photoelectric yield (23.7 eV).⁷⁰ Using the value for the optical band gap $(14.2 \pm 0.2 \text{ eV})^{71, 72}$ the F 2s band is placed at about 38.2 ± 0.8 eV below the conduction band threshold. We would expect the $F^{-}2s$ excitons to lie below this energy and the interband F⁻ 2s-to-conduction transitions to lie appreciably higher in energy, i.e., somewhat above

50 eV. The absorption spectra in the 35-50 eV region⁶³ show no structure. The energy-loss spectra calculated⁷⁹ from these data show only plasmon peaks at 45 and 50 eV, while the measured energy-loss spectra^{77,78} show also two pronounced structures at 33.5 and 42 eV and an additional feature at 51 eV. Absorption in the 50-60 eV region shows a flat structure which was tentatively assigned to a Li 1s transition. Due to the possible overlap of the high-energy part of the valence to conduction bands with the low-energy part of the Li 1s transitions, it is difficult to resolve the spectra in the 35-50 eV region. The inelastic electron scattering data of Fields et al.⁸⁸ reveal a forbidden $F^{-}2s$ exciton at 35 eV (i.e., 2.6-eV binding energy) which is probably due to a $F^{-}(2s)$ -Li⁺(2s) pair below the conduction band threshold.

(iv) The fundamental valence-conduction region. Roessler and Walker⁶⁰ measured the reflectance of LiF in the 10–20 eV region and analyzed the data in terms of a $F^{-}(2p) \rightarrow \Gamma_{1,c}$ exciton at 12.6 eV and a gap of 13.6 eV. Piacentini⁷² has analyzed the absorption peak around 12.6 eV in terms of a single asymmetric Lorentzian, suggesting that a single excitation is responsible for this exciton. Using an effective-mass model, the exciton series was found to converge to $E_g = 14.2$ eV and to show pronounced central-cell corrections for the short-range n=1 exciton at 12.6 eV. A similar treatment by Piacentini *et al.*⁷¹ of their thermoreflectance data yielded virtually the same results, indicating a binding energy of about 2.1 eV for the n=1 exciton and an effective exciton radius of 1.9 Å. Metzger 62 observed the photoelectric yield in LiF and found the exciton photoemission to start at 12.3 eV and a photoemission minimum at about 14 eV to mark the onset of the conduction band. Similar studies by Pond and Inouye⁸⁹ indicated a photoelectric threshold at 12.6 ± 0.3 eV for incident photon energies in the exciton range and a lower edge of 11.8 ± 0.3 eV for higher $(h\omega > 15 \text{ eV})$ photon energies, the latter most probably being due to an $F^- 2p$ surface state lying above the intrinsic valence band edge. This study also established the base width of the F⁻ 2pvalence band to be 4.6 ± 0.3 eV which is somewhat smaller (~ 6 eV) than that determined previously by XPS.^{61,90}

Having tentatively identified the main interbandtype features in the LiF spectra, we may now compare the predictions of the band model with the observed data. Table V shows some of the main structures observed together with the values obtained using the difference between eigenvalues calculated from our band structures both for the exchange and correlation model ($\alpha = \frac{2}{3}$) and the exchange model with a scaled exchange parameter ($\alpha = 1$) (columns 3 and 4). The upper three entries in Fig. 8 show graphically the calculated positions of the Li⁺ 1s and F⁻ 2s excitations as compared with the observed data.

TABLE V. Calculated transition energies (in eV) in LiF using the band model with: (i) exchange $(\alpha = \frac{2}{3})$ and correlation and (ii) exchange $(\alpha = 1)$ only, compared with the crystalline Δ SCF exchange $(\alpha = \frac{2}{3})$ correlation model and the observed data. The experimental uncertainties and assignments are discussed in Sec. IV A. V indicates vacuum. The letters in the last column refer to the assignment discussed in the text and in Fig. 8.

Transition	Туре	Band $\alpha = \frac{2}{3}$	models $\alpha = 1$	Crystal ∆SCF	Expt
$\Gamma_{15,v} \rightarrow \Gamma_{1,c}$	Interband p exciton	9.8	10.5	13.9 11.7	$14.2 \pm 0.2 \\ 12.6 \pm 0.2$
$\Gamma_{15,v} \rightarrow V$	Ionization	10.2	11.7	14.3	13-14
$F^{-}(2s) \rightarrow \Gamma_{1,c}$	Interband s exciton	27.9	31.3	37.0 34.1	37.9 35.0
$\mathbf{F}^{-}(2s) \rightarrow V$	Ionization	30.1	32.5	37.2	(X) 37.6
$\operatorname{Li}^+(1s) \rightarrow \Gamma_{1,c}$	Interband s exciton	47.2	57.2 	$\begin{array}{c} 63.3\\ 61.3\end{array}$	64.4±0.8 (A)60.8
$\mathrm{Li}^+(1s) \to V$	Ionization	47.6	58.4	63.5	64 ± 0.2
$\mathrm{Li}^+(1s) \!\rightarrow\! L_{1,c}$	Interband	49.6	59.5	65.2	(B) 64.9
$\mathrm{Li}^+(1s) \mathop{\rightarrow} L_{2,c}$	Interband	55.1	64.9	67.9	(C) 67.4
$\text{Li}^+(1s) \rightarrow L_{3,c}$	Interband p exciton	58.1 •••	68.5 •••	$71.4\\62.2$	(D) 69.6 (A) 61.9
$F(1s) \rightarrow V$	Ionization	655.2	680.9	694.5	693.2



FIG. 8. Fluorine 2s and Lils excitation spectra. Here -- denotes interband transitions, — denotes excitons, and $-\cdot$ - the vacuum level. The notation A', A, B, C, X, and D refer to spectral lines discussed in the text. The top two entries denoted $\Delta \epsilon$ refer to band model calculations.

Our results for $\alpha = 1$ agree very well with those previously published by Menzel et al.¹⁶ and Chaney et al.,¹⁷ as indicated above. Note that in these calculations the position of the vacuum level is rather accurately determined from the solution of the one-particle equation and there is no justification in shifting the calculated eigenvalue difference arbitrarily so as to match some experimental lines. Both the present LDF and Menzel's et al. calculation are highly converged with respect to basis-set expansion, are fully self-consistent, and employ the full crystalline potential with no shape approximations. Thus they are believed to provide solutions to the one-particle equations with accuracy of 0.1 eV or better. The agreement of the calculated band-structure predictions and the experimental data is seen to be very poor over the entire spectral region: the band model underestimates the observed transition energies by as much as 4 eV in the valence region and up to 38 eV in the deep core region. An artificially increased exchange coefficient of $\alpha = 1$ seems to produce somewhat better agreement with experiment but still leaves very large discrepancies.⁹¹

B. Crystal Δ SCF model

In order to examine the reasons for the breakdown of the simple *eigenvalue-difference* approach to the excitation energies in the LDF model, we consider a more exact approach, namely, the Δ SCF method in which the transition energy is calculated as the *difference in total energy* for two independent SC calculations for the ground and excited state. We recall that when the electron-gas model is used to approximate the total exchange and correlation energy functional $E_{xc}(\rho(\vec{r}))$ the crystal potential for the *N*-electron system is given by²

$$V_{\rm LDF}^{(N)}(\vec{\mathbf{r}}) = \sum_{m,\alpha} \frac{-Z_{\alpha}}{|\vec{\mathbf{r}} - \vec{\mathbf{R}}_m - \vec{\mathbf{d}}_{\alpha}|} + \sum_{j=1}^N n_j \int \frac{\rho_i(\vec{\mathbf{r}})}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|} d\vec{\mathbf{r}}' + \left(\epsilon_{xc}(\rho(\vec{\mathbf{r}})) + \frac{d\epsilon_{xc}(\rho(\vec{\mathbf{r}}))}{d\rho(\hat{\mathbf{r}})}\right), \qquad (2)$$

where $\rho_j(\vec{r}) = \psi_j^*(\vec{r})\psi_j(\vec{r})$ is the *j*th orbital density (here *j* denotes both the band and the wave-vector index) and the total density is given by $\rho(\vec{r}) = \sum_{j=1}^{N} n_j \rho_j(\vec{r})$ and n_j is the occupation number. We note that the direct electronic Coulomb term [second term in Eq. (2)] includes the self-interaction energy for the electron in the *j*th orbital and that unlike the case of the Hartree-Fock model, the exchange-correlation terms [third term in Eq. (2)] do not cancel exactly this self-interaction. The use of this potential in a local density variational treatment leads to an *N*-electron total energy of the form^{2,92}:

$$E^{(N)} = \sum_{i} n_{i} I_{i} + \frac{1}{2} \sum_{i, j} n_{i} n_{j} F_{ij}$$
$$+ \int \sum_{i} n_{i} \rho_{i}(\vec{\mathbf{r}}) \epsilon_{xc}(\rho(\vec{\mathbf{r}})) d\vec{\mathbf{r}}, \qquad (3)$$

where the one- and two-electron integrals I_i and F_{ij} , respectively, are given by

$$I_{i} = \int \rho_{i}(\vec{\mathbf{r}}) \left(-\frac{1}{2} \nabla^{2} - \sum_{m, \alpha} \frac{Z_{\alpha}}{|\vec{\mathbf{r}} - \vec{\mathbf{R}}_{m} - \vec{\mathbf{d}}_{\alpha}|} \right) d\vec{\mathbf{r}}, \quad (4)$$

$$F_{ij} = \int \int \frac{\rho_{i}(\vec{\mathbf{r}}) \rho_{j}(\vec{\mathbf{r}}')}{|\vec{\mathbf{r}} - \vec{\mathbf{r}}'|} d\vec{\mathbf{r}} d\vec{\mathbf{r}}'. \quad (5)$$

The *l*th eigenvalue of the LDF-one-particle equation [Eq. (1)] is given as the average of $-\frac{1}{2}\nabla^2 + V_{\text{LDF}}^{(N)}(\vec{r})$ over the *l*th orbital density:

$$\epsilon_{l}^{\text{LDF}} = I_{l} + \sum_{j} n_{j} F_{jl} + \int \rho_{l}(\vec{\mathbf{r}}) \left(\epsilon_{xc}(\rho(\vec{\mathbf{r}})) + \rho(\vec{\mathbf{r}}) \frac{d\epsilon_{xc}(\rho(\vec{\mathbf{r}}))}{d\rho(\vec{\mathbf{r}})} \right) d\vec{\mathbf{r}}.$$
 (6)

Again, the Coulomb self-interaction term F_{11} is not exactly canceled by the self-exchange term. An extreme case occurs in the LDF treatment of the hydrogen atom in which the $F_{1s,1s}$ term is not canceled exactly by the last term in (6) (due to the lack of other particle exchange terms). Instead, only a partial compensation is exhibited.⁴

We consider now the ionization energy of the electron from the *I*th band in the crystal as a total energy difference. In the lowest level of approximation, one assumes that all the eigenfunctions of the system are unchanged (relative to the ground state) by the removal of a single electron from the system (unrelaxed or "frozen orbital" limit). Hence, one expands the total energy difference $E^{(N-1),0} - E^{(N),0}$ (where the zero superscript denotes ground-state eigenvectors) in a Taylor series with respect to the population numbers in a standard way and finds to second order:

$$E_{I}^{(N-1),0} - E^{(N),0} = -\epsilon_{I} + \Pi_{II}^{0}, \qquad (7)$$

where the unrelaxed first-derivative $\partial E_i^{(N),0}/\partial n_i$ equals the negative of the eigenvalue ϵ_i and the nondiagonal second-order term (unrelaxed self-interaction) is given by

$$\Pi^{0}_{II'} = F^{0}_{II'} + \int \left(\rho^{0}_{I} \left(\vec{\mathbf{r}} \right) \frac{\partial \epsilon_{xc} \left[\rho^{0} \left(\vec{\mathbf{r}} \right) \right]}{\partial n_{I}} + \rho^{0} \left(\vec{\mathbf{r}} \right) \frac{\partial^{2} \epsilon_{xc} \left[\rho^{0} \left(\vec{\mathbf{r}} \right) \right]}{\partial n_{I} \partial n_{I'}} + \rho^{0}_{I'} \left(\vec{\mathbf{r}} \right) \frac{\partial \epsilon_{xc} \left[\rho^{0} \left(\vec{\mathbf{r}} \right) \right]}{\partial n_{I'}} \right) d\vec{\mathbf{r}}$$
(8)

with higher-order corrections which are proportional to $\partial^{p} E^{(N),0} / \partial n_{l}^{p}$ for $p \ge 3$. Hence, one observes that, contrary to the situation prevailing in the HF model, the unrelaxed total energy difference does not equal the negative of the corresponding eigenvalue alone and that an addition term appears. (This term measures the change in the energy of the *l*th eigenvalue upon removal of an electron from the system due to the diminished screening by the remaining electrons and removal of its self-interaction.) Numerical estimates for the screened self-interaction term Π_{II}^{0} in atoms obtained by calculating the left-hand part of Eq. (7) with ground-state orbitals] indicate that it is positive (i.e., $-\epsilon_{l} + \prod_{ll}^{0}$ yields a *higher* ionization potential than Koopmans value $-\epsilon_1$ and decreases in absolute magnitude in going from deep shell orbitals to the outer valence orbitals. $^{\rm 93-98}$ $\,$ For the ionization of the 1s electron in the $Li^{+}1s^{2}$ case, this term amounts to about 19 eV $(E^{(N),0} - E_{1s}^{(N-1),0})$ = 77.4 eV; $-\epsilon_{1s}$ = 58.4 eV).

In a higher level of approximation, one allows the orbitals in the excited state to relax variationally, thereby lowering the excitation energy. One defines the relaxation-polarization self-energy $\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{$

$$\Sigma_{i}^{*} = (E_{i}^{(N-1),*} - E_{i}^{(N),0}) - (E_{i}^{(N-1),0} - E_{i}^{(N),0})$$
$$= E_{i}^{(N-1),*} - E_{i}^{(N-1),0}, \qquad (9)$$

where the superscript asterisk denotes the use of self-consistently determined wave functions in the variationally calculated excited-state total energy. Note that this definition is slightly different from other definitions⁸⁷ in that relaxation in Π_{11}^0 is incorporated here in Σ_1^* . Numerical estimates of Σ_1^* for occupied orbitals in atoms indicate that it is negative and usually much smaller in absolute magnitude than Π_{11}^0 (e.g., -2 eV for Li⁺ 1s). Similar results for relaxation-polarization self-energies for atoms are obtained in the HF model⁸⁵⁻⁸⁷⁻⁹⁵ and in linearized LDF models. Note that Σ_1^* in Eq. (9) is not explicitly dependent on the wave vector.

The final expression for the \triangle SCF ionization energy,

$$\Delta E_{l} = E_{l}^{(N-1), *} - E^{(N), 0} = -\epsilon_{l} + \Pi_{ll}^{0} + \Sigma_{l}^{*}, \qquad (10)$$

can be generalized to excitation energies between states l and λ in the limit of zero electron-hole interaction as

$$\Delta E_{\lambda I} = E_{\lambda}^{(N), *} - E_{I}^{(N), 0}$$
$$= \Delta \epsilon_{\lambda I} + (\Pi_{\lambda \lambda}^{0} - \Pi_{II}^{0}) + (\Sigma_{\lambda}^{*} - \Sigma_{I}^{*}). \quad (11)$$

We note that both the self-interaction and the relaxation-polarization self-energy terms depend on all the electrons in the system and not only on the particular pair occupying the λ , *l* states. In this limit, the "rigid" band-structure model which treats the *l* to λ excitation energy as $\Delta \epsilon_{\lambda l}$ no longer holds and a separate treatment is needed for each individual transition. Equation (11) for the excitation energy is pertinent to the situations where the excited electron and hole are allowed to polarize the remaining electrons and to relax their own electronic states but have a zero Coulomb and exchange-correlation interaction between themselves (i.e., they both occupy delocalized Bloch states). In the limit where these particles maintain any degree of localization and hence, interact directly (as in an exciton state) the excitation energy is given by

$$\Delta E_{\lambda l} = \Delta \epsilon_{\lambda l} + (\Pi^{0}_{\lambda \lambda} - \Pi^{0}_{l l}) + (\Sigma^{*}_{\lambda} - \Sigma^{*}_{l}) - K^{e, h}_{\lambda l}, \quad (12)$$

where $K_{\lambda l}^{e, h}$ is the interaction between the electron at λ and the hole at *l*. Equation (10) is thus pertinent to the description of photoionization while Eqs. (11) and (12) are pertinent to the description of itinerant interband transitions and exciton states, respectively. One notes that the application of the standard band model for excitation energies (i.e., joint density of states) relies on the assumption that, for an excitation of a single electron in the solid, the self-interaction, relaxation polarization self-energy, and electron-hole interactions are small (of the order of 1/N, where N is the total number of particles in the system). One notes, however, that although the self-interaction and self-energy effects are generally expected to decrease in importance as we go from atoms to molecular clusters and finally to solids, this decrease is by no means monotonic with the system's size and excitations which give rise to localized states can certainly exist in extended systems.

Several approaches have been previously at-

tempted to calculate the relaxation-polarization self-energy and the electron-hole interactions in solids. Those involve either atomic models^{85,86} (in which the corresponding effects are calculated in atoms and then added as a constant to the bandstructure estimate of $\Delta_{\epsilon_{\lambda l}}$) or more extensive solid-state approaches⁹⁹ (that involve a model treatment of the exchange screening and electronhole interaction). One notes that in the former approach one assumes that the relaxation effects in the crystal are unscreened relative to the freeions and that the unperturbed extended crystal states experience the same relaxation, correlation, and electron-hole effects as the localized electron-hole pair (i.e., the calculated Δ_{ϵ} in an entire spectral region is shifted by $\Sigma^* + K_{ii}$ corresponding to a single selected transition i - j). Free-ion models,¹⁰⁰ on the other hand, neglect the detailed band-structure effects on the transition energies (i.e., the proper solid-state short-range Coulomb and exchange correlation potentials and wave-function overlap). Further, the self-energy terms are directly transferred from the observed free-ion excitation energies, and thus neglect the effects of solid-state screening and valence band polarization. Effective-mass²¹ and Frenkel-type²² models for localized excitations in solids neglect, in low order, relaxation effects and assume the range of localization of the state in question (as long-range and short-range, respectively).

Our objective is to use a \triangle SCF model [i.e., Eqs. (10)-(12)] directly for the solid. Since we are unable to start from a Bloch Hamiltonian and obtain localized-like solutions as a particular case,^{101,102} our basic approach is to assume symmetry breaking by making a localized excitation at a given site in the crystal and to observe whether the screening accompanied by the self-consistent charge redistribution would be sufficient to keep the energy of this state within the continuum of the unperturbed states (in which case the state would mix with the nearby states of the same symmetry to form an itinerant manifold that would be describable by the conventional band-structure approach) or if the localized description (i.e., a split-off energy level with exponentially decaying wave-function amplitudes) would persist. When an electron having an average Coulomb parameter U (Ref. (101) is excited from a band of width W, such that $U/W \gg 1$, we might expect that a localized state would indeed finally form, and that in the \triangle SCF picture it would be stabilized by the removal of its self-interaction term and be appreciably affected by relaxation and polarization effects. The \triangle SCF model is hence complementary to the one-electron band model in that such localized states become possible. Thus we treat the locally excited species as a

point-defect interacting with the bulk crystalline states and seek a self-consistent solution for the total energy of that system in the LDF model; its difference from the total ground-state energy comprises our Δ SCF estimate of the corresponding excitation energy, with the effects discussed in Eqs. (10)-(12) included.

Several well-known techniques are available for treating point defects in solids: The Slater-Koster¹⁰³ and molecular-cluster models¹⁰⁴ are perhaps too crude in that the former severely restricts the range of the perturbative potential and does not lend itself in an obvious way to self-consistency, while the latter introduces unphysical surface states and does not contain a realistic description of the bulk band states (e.g., band edges, etc).

One of us has previously suggested a different model for treating such point-defect problems, namely, the small-periodic-cluster (SPC) model^{19,20} in which one constructs a large crystallographic unit cell with a defect placed at its center and solves the associated Bloch Hamiltonian problem (with periodicity imposed with this large supercell) using band-structure techniques. To the extent that the defect-defect interaction present in this superlattice model (monitored by the dispersion of the defects one-electron band) can be kept small by choosing a sufficiently large SPC, the solution would form a good approximation to that of a single point defect in the lattice. In the case of LiF, we use a basic unit cell containing 8 (fcc structure) or 16 (simple cubic structure) atoms, with one of them being locally excited (and the defect-defect distance is a and $\sqrt{2}a$, respectively, where a is the lattice constant). One obtains the \triangle SCF estimate for the excitation energies simply by substracting the ground-state energy from that of the defectcontaining crystal model.

The main physical contents of our periodic cluster \triangle SCF model include: (i) Contrary to free-ion models,¹⁰⁰ "band structure" effects such as the detailed influence of the crystal potential and the variationally determined crystalline wave functions on the one-electron spectra $\Delta \epsilon_{\lambda I}$ are directly incorporated. (ii) Spurious self-interaction effects present in the LDF band model are largely eliminated by treating directly *total* energy rather than eigenvalue differences. (iii) Excited-state orbitals are allowed to self-consistently relax in response to the perturbed crystal potential and similarly the band states are properly polarized by the existing hole state. This may be compared with atomiclike self-energy models^{85,86} which do not incorporate solid-state effects for these quantities. (iv) Electron-hole interaction is directly affected via both the Coulomb and the exchange-correlation interaction present in the basic LDF Hamiltonian.

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The local-field screening of this interaction is determined naturally in the SC cycle without invoking an extraneous semiclassical electron-hole interaction law.^{86,87} (v) A large number of crystal states and ionic sites are allowed to interact nonperturbationally in forming the final defect state. The range of localization of these states is not assumed (except as an initial input to the SC cycle) but comes out rather naturally from the model. This may be compared with simplified Slater-Koster one-site one-band models^{85,86,103} and with the molecular-cluster approach¹⁰⁴ which involve a limited basis for the interacting system. (vi) The "point-defect" wave functions are naturally matched with the appropriate unperturbed Bloch states through the use of a basis set which is a superlattice of crystal functions with Bloch periodicity. The solutions obtained for a given hole state are orthogonal to all other Bloch-like solutions. This seems to offer a distinct advantage over methods that treat differently (and separately) resonating versus localized defect states.¹⁰⁵

The main disadvantages and limitations of the superlattice \triangle SCF model are:

(a) Only excitations giving rise to reasonably localized defect wave functions (localization range of 1–2 lattice constants) can be efficiently treated. Large radius (Wannier-type)excitons or discrete excitations resonating in the conduction band continuum are characterized by slowly decaying tails and produce non-negligible defect-defect interactions. These are better described by effectivemass models,²¹ perturbative approaches,¹⁰⁶ or integral equation methods¹⁰⁷ that use the perfect crystal Bloch states as a zero-order basis. On the other hand, all core excitations and the rapidly screened valence hole states in metals and insulators should be amenable to a realistic description by this model.

(b) A ground-state LDF calculation of the total energy in the presence of a hole does not guarantee, in principle, a variational upper bound even with the correct exchange and correlation functional. Since we are unable to find a physically reasonable localized excited mode from an *unrestricted* solution to the (N-1)-particle LDF equations, we are forced to consider a fictitious external potential² that would keep the hole in a given subband. Although this seems to be a reasonable model, the Δ SCF excitation energies probably form upper bounds to the correct result because of the absence of a truly variational description of the excited state.

(c) Certain dynamical contributions to the selfenergy associated with higher-order perturbative terms^{95,99} (not appearing in the ground-state LDF equations) are ignored (e.g., a configurational interaction between quasidegenerate excitations of the same symmetry). These are usually smaller than the direct self-energy and relaxation-polarization terms for the system in question and should be viewed as refined corrections to our results. Since their relative contribution seems to increase for outer-shell excitations, one expects the super-lattice Δ SCF model to work better for inner shells.

(d) Our spin-restricted model neglects multiplet splittings in the calculated spectra. These are unresolved experimentally in LiF but are apparent in other members of the alkali-halide series.

(e) The \triangle SCF model does not guarantee the orthogonality of the all-electron excited hole state to all other hole states produced by different excitations since they are constructed from different LDF Hamiltonians. In practice, however, orthogonality is maintained to within reasonable accuracy (e.g., the overlap integral between fluorine 2s and 1s hole wave functions in LiF crystal is 2×10^{-3}) due to the occurrence of the hole in a distinctly different subshell in each case. The orthogonality of a given hole state to all other one-particle bandlike states is guaranteed in the \triangle SCF model since the same Hamiltonian generates all these states.

V. RESULTS FOR THE Δ SCF EXCITATION ENERGIES

The local perturbations assumed in this study are classified into three groups, depending on the nature of the excitation being investigated:

(i) Local-to-ilinerant transitions. We consider three particular examples: the two core-to-conduction transitions $\text{Li}^{+}(1s) \rightarrow \Gamma_{1,c}$ and $\text{Li}^{+}(1s) \rightarrow L_{3,c}$ and the valence-to-conduction transition $F^{-}(2p^{6})$ $-\Gamma_{1,c}$. In the first two, the 1s subshell of a given Li site is excited into either the bottom of the conduction band $\Gamma_{1,c}$ (having 97% Li 2s character, as judged from the population analysis of the computed band eigenfunction) or to the $L_{3,c}$ state, lying some 10 eV above the bottom of the conduction band (and having 93% Li 2p character). In the third example, we excited a 2p subshell of a given F⁻ site into the bottom of the conduction band at $\Gamma_{1,c}$. For these excitations, we view the final state as an itinerant Bloch state while the initial state contains a locally excited site. We prepare an initial crystal potential for these states in the following way: for the two core excitations we generate a superposition density (and a corresponding potential) by creating a hole in the 1s shell of a particular Li site (i.e., $Li^{2+} 1s^1 2s^0 2p^0$) and place the excited electron either in the Li 2s orbitals of all other Li sites in the unit cell (i.e., $Li^{(1+1/N)+}$ $1s^2 2s^{1/N} 2p^0$, N being the number of Li sites in the cell) or in all of the Li 2p orbitals (i.e., Li^{(1+1/N)+} $1s^22s^02p^{1/N}$ for the transitions to the $\Gamma_{1,c}$ and $L_{3,c}$

final states, respectively. Using these *initial* crystal potentials we perform a fully self-consistent band-structure calculation *subject to the constraint that the* (*lowest*) Li *Is band contains*, *on the average, one hole* (i.e., 2N-1 electrons, for both spins). Hence, the initially localized hole state is allowed to relax its own orbitals, to polarize the rest of the states, and to delocalize spatially under the influence of the self-consistent crystal potential subject to the restriction that it remains in the 1s band. For the $F^-(2p^6) + \Gamma_{1,c}$ transition, we prepare a crystal potential corresponding to a 2p hole in a particular F site (i.e., F^0 $1s^22s^22p^5$) and a spread-out electron in the Li 2s

shell (i.e., $\operatorname{Li}^{(1+1/N)+} 1s^2 2s^{1/N} 2p^0$). (ii) Localized to localized transitions: Here we consider the possibility of the formation of $Li^{+}(1s - 2s)$, $Li^{+}(1s - 2p)$, and $F^{-}(2p) - Li^{+}(2s)$ excitons. For the first two we prepare a crystal potential corresponding to SPC's with one Li atom in the Li⁺ $1s^12s^12p^0$ or the Li⁺ $1s^12s^02p^1$ configurations (for the exciton states of s and p symmetries, respectively) while the rest of the unit cell atoms are in their "normal" $Li^+ 1s2s^02p^0$ and F $1s^22s^22p^6$ states. These locally excited species correspond to the one-site Li core excitons. For the two-site $F^{-}(2p)$ -Li⁺(2s) optical exciton, we construct a crystal potential for an SPC with one F site in the $F^0 1s^2 2s^2 2p^5$ configuration and a nearestneighbor Li site in the Li⁰ $1s^22s^12p^0$ configuration, with the rest of the atoms in their "normal" state. With these starting potentials, we perform selfconsistent band-structure calculations restricting the Li 1s and F 2p bands to have 2N - 1 electrons.

(iii) *Ionization*. In considering an ionization process we form a hole in a given ion site (e.g., F^0 $1s^{1}2s^{2}2p^6$ or $Li^{2*} 1s^{1}2s^{0}2p^0$ for $F^- 1s$ and Li^*1s ionizations, respectively) and perform a (non-neutral) calculation using this crystal potential.

For each of the initial crystal potentials we prepare an independent set of trial Bloch functions

$$\tilde{\Phi}_{\mu\alpha}(\vec{\kappa},\vec{r}) = \sum_{n} e^{i\vec{\kappa}\cdot\vec{\tau}_{n}}\chi_{\mu}(\vec{r}-\vec{\tau}_{n}-\vec{d}_{\alpha}), \qquad (13)$$

where \vec{k} denotes a wave vector in the (small) BZ constructed from the large direct-space supercell (in the case of an unperturbed SPC, each of these \vec{k} 's is reducible to N values of \vec{k} in the primitive zone, e.g., for 4 molecules per cell, $\vec{k}=0$ corresponds to $\Gamma + 3X$ in the small BZ representation) and $\vec{\tau}_n$ denotes a direct lattice vector for the supercell. To allow for greater flexibility of our basis, we compute the set $\chi_{\mu}(\vec{r} - \vec{d}_{\alpha})$ self-consistently (and numerically) for the free-ion species assumed in our initial potential construction (e.g., for the local ionization of a Li^{*} 1s electron from the solid our basis set contains orbitals computed selfconsistently for the $Li^{2+} 1s^{1}2s^{0}2p^{0}$ ion, together with those computed for the regular Li⁺ $1s^22s^02p^0$ and $F^{-} 1s^2 2s^2 2p^6$ ions). Thus a large part of the orbital radial distortions accompanying the charge redistribution in the solid upon ionization is already affected by these nonlinearly optimized orbitals. The relaxation introduced by other sites is allowed for through the solution of the linear variation problem. In subsequent iterations, where the population analysis of the crystal eigenfunctions indicates a population change in any of the basis functions by more than about |0.2|e, these basis functions are recomputed from the free-ion onesite LDF equations using the updated orbital population of the corresponding ion. This technique offers an important advantage over standard LCAO methods employing a fixed set of orbitals throughout the calculation and improves substantially the convergence rate of the SC cycle [2-4] iterations for core excitations and 4-6 iterations for valence excitations are required to obtain an agreement of $\delta \leq 10^{-2}e$ between the input and output unit-cell charge-density averages: $\delta = \int_{UC} |\rho_{out}(\vec{r})|$ $-\rho_{in}(\mathbf{\tilde{r}}) | d\mathbf{\tilde{r}} |$. The excitation energies obtained in this manner are depicted in Table V together with the experimental data. Figure 8 presents schematically the positions of the Li 1s and F 2s excitations and their relation to the one-electron bandstructure results.

A. Li 1s excitations

The calculated Li 2s spectra start with two exciton states: the forbidden Li 1s-2s at 61.3 eV and the allowed Li 1s-2p at 62.2 eV, and is followed by the onset of the interband transitions and the ionization limit at 63.3 and 63.5 eV, respectively. The s and p exciton binding energies are 2.0 and 9.2 eV, respectively (measured relative to the corresponding s and p band states $\Gamma_{1,c}$ and $L_{3,c}$). Past the series limit we find the interband region (for which we have computed those transitions giving rise to peaks in the density of states¹⁶ such as to the $L_{1,c}$, $L_{2,c}$, and $L_{3,c}$ states) extending to about 71 eV.

The calculated Li s and p exciton energies agree very well with the inelastic electron scattering⁸⁸ and the optical data, ^{65-67,74} but are in conflict with the suggestion of Kunz *el al.*^{86,87} that the s exciton lies at 54 eV. Our calculation indicates that similar to the situation prevailing in the exciton spectra of the rare-gas solids,⁸² the position of the Li 1s core exciton is only slightly shifted (0.2–0.3 eV) with respect to the corresponding free-ion transition. On the other hand, the calculations of Kunz *et al.*^{86,87} and Collins *et al.*⁸⁵ suggest that the Li s exciton lies some 7 eV lower than the corresponding transition in the ion, while the energy of the Li p exciton almost coincides with the position of the free-ion transition. Since the orbital relaxation accompanying the cation core excitations is almost entirely localized at the excited site (this being a single-site exciton) and crystal screening is expected to be minor due to the small valence charge on the Li sublattice, only solid-state correlation effects are expected to give rise to the difference between the crystal and free-ion localized excitation energy. Various model calculations^{26,108} indicate that these correlation corrections are far smaller than the difference in solidstate versus free-ion core excitations energies as found by Kunz et al.^{86,87} We further note that in their treatment of Li core correlation effects, the semiclassical Mott-Littleton correction (3.0 eV) is included on top of the similar long-range polaron contribution (3.5 eV) and yields a highly improbable value for the Li 1s ionization energy (57 eV compared with the measured value of 64 ±0.2 eV).59

Similarly, our results are in direct contradiction with those of Menzel *et al.*¹⁶ which suggest that the *band structure* derived eigenvalue difference, $\epsilon_{L_{3,c}} - \epsilon_{L_{1,1s}}$, would be identified with the experimental absorption threshold (peaks A' and A) and thus dismiss the occurrence of core excitons in the spectra. Our results (Table V) show that not only is the *interband* transition energy changed by as much as 13 eV upon the removal of the self-interaction terms and the introduction of relaxation-polarization effects, but that in addition a stable *exciton* state appears some 9 eV below this threshold when a locally screened self-consistent electron-hole interaction is allowed.

In order to study the evolution of a localized state in the solid and its relation to similar states in the free ion, we have calculated the changes in charge density brought about by localized excitations in both systems. Figure 9 shows the difference in radial orbital density $\Delta \rho(\mathbf{\tilde{r}})$ between a lithium ion with a hole in its 1s shell and a groundstate lithium ion, as calculated from the two corresponding SC solutions. The area under each of these curves is zero since $\Delta \rho(\mathbf{\tilde{r}})$ is taken as the difference between two normalized orbital densities. It is seen that upon forming a core hole, substantial 1s density is concentrated in a region close to the nucleus ($R \le 0.6$ a.u.) while an equal amount of charge is deleted from the outer part $(0.6 \le R \le 2.5 \text{ a.u.})$; note that the total perturbation decays to zero at a distance shorter than the nearest-neighbor ion in the solid. On the other hand, the 2s and 2p orbitals undergo much stronger re-



FIG. 9. Orbital density differences in the lithium shells induced by formation of a 1s hole as calculated from two independent LDF SC calculations. The full dots indicated the positions of the ions in the solid.



FIG. 10. Core charge density differences due to Li 1s hole formation in the solid. $\Delta \rho_{\rm NSC}^{\rm ery}(r)$ and $\Delta \rho_{\rm SC}^{\rm ery}(r)$ denote the results obtained in non-SC and SC calculations, respectively, while $\Delta \rho^{\rm ion}(r)$ is the core free-ion hole density.

laxation effects and become substantially more localized than in the unperturbed ion. Whereas the orbital relaxation effects shown in Fig. 9 are totally neglected in the band-structure approach¹⁶ to excitation energies, free-ion models⁸⁵⁻⁸⁷ at the other extreme, assume that this free-ion $\Delta\rho(\mathbf{\hat{r}})$ persists in the solid in an unscreened fashion.

Figure 10 shows the calculated difference in the crystal 1s radial charge density along the [100] direction, obtained from two independent [non-SC and SC) supercell calculations (curves labeled $\Delta \rho_{\text{NSC}}^{\text{cry}}(\mathbf{\tilde{r}})$ and $\Delta \rho_{\text{SC}}^{\text{cry}}(\mathbf{\tilde{r}})$, respectively]. To facilitate comparison with the free-ion case, only the charge density difference contributed by the central Li site is shown. The curve labeled $\rho^{\text{ion}}(\mathbf{\tilde{r}})$ shows the perturbation $\rho_{1s}(Li^{2+}) - 2\rho_{1s}(Li^{+})$ calculated from the free-ion densities. [The area under these curves is -1 since $\rho(\mathbf{\vec{r}})$ is defined here as total 1s charge density differences.] Comparing the $\rho_{\rm NSC}^{\rm cry}({\bf \tilde{r}})$ and $\rho^{\text{ion}}(\mathbf{\vec{r}})$ curves, it is seen that the hole density in the free-ion case is only slightly modified when put in the crystal environment (this is not surprising since the basis functions used to describe the hole state in the crystal are generated from exact hole-state functions in the ion). When self-consistency is achieved, the shape of the hole density changes is flattened slightly (mainly due to screening by the small admixture of Li 2s and 2p states into the valence band) but remains largely localized on the perturbed site and shows negligible overlap with the nearest-neighbor sites. Thus this 1s core hole is more logically describable in terms of freeion models; crystal effects introduce only a small shift due to the diminished relaxation. Since almost all of the valence charge in LiF is localized on the fluorine sublattice, the screening of the Li 1s hole in the solid is ineffective and the free-ion

hole persists. Due to the short range of the perturbation introduced by the core hole (Fig. 10), our superlattice representation does not reveal any unwarranted defect-defect interaction and the results obtained with an 8-atom and 16-atom SPC are identical to within numerical accuracy. The main difference between the free-ion and crystal Li core hole density is brought about by the admixture of some 2s and 2p orbitals into the occupied manifold of the latter; while the large changes in these radial densities upon hole formation (Fig. 9) does not affect the shape of the freeion hole, they give rise to some structure in the total hole density (i.e., 1s, 2s, and 2p) in the solid. From these results, it is apparent that the dramatic breaking of the lattice symmetry by the formation of a localized hole (Fig. 10) casts serious doubt on the (unperturbed) band-structure approach to core excitation energies. Similarly, the solidstate hybridization effects on the hole density may introduce (probably smaller) errors into the freeion models.

The transition between the Li core state and the (high density of states) conduction-band levels $L_{1,c}, L_{2,c}$, and $L_{3,c}$ calculated to appear at 65.2, 67.9, and 71.4 eV, respectively, agree well with the experimental peaks B, C, and D observed⁷⁴ at 64.9, 67.4, and 69.6 eV, respectively (cf., Fig. 8). These excitations into p-like conduction states are subjected to strong perturbations by the presence of the Li hole state. Thus the \triangle SCF model for these transitions not only shifts their positions relative to the band-structure prediction (cf., Fig. 8) but their *relative* locations also change (e.g., the transitions to $\Gamma_{1,c}$ and $L_{3,c}$ have a separation of 10.9 eV in the band-structure model while the \triangle SCF model shows a splitting of only 8.1 eV between these transitions). Thus we conclude that the relaxation-polarization and electron-hole interaction effects cannot be applied to a band structure as a rigid shift, in disagreement with the suggestion of Kunz et al.86,87

B. F(1s) and F(2s) excitations

The calculated fluorine 2s spectra start with a forbidden two-site $F^{-}(2s) - Li^{+}(2s)$ exciton at 34.1 eV and are followed by the interband threshold and the ionization limit at 37.0 and 37.2 eV, respectively. Past this threshold we expect interband absorption bands which have appreciable intensity only at energies where fluorine final states exist. Our calculations indicate that such transitions would start at about 50 eV (i.e., about a Rydberg above the conduction threshold) where the $\Gamma_{12,c}$ and $\Gamma_{25,c}$ states become accessible. Indeed, the absorption spectra in this region^{63,73} does show a wide

window between the conduction threshold at 38 eV and about 50 eV where a weak structure occurs.^{64,67} Although previously attributed to the Li 1s spectra,^{16,75,76,84-87} our present study suggests that this might be a F^- 2s-to-conduction interband transition. The correlated HF calculations of Kunz⁸⁷ predict an $F^{-}(2s)$ exciton at 37.6 eV (i.e., only 0.3-eV binding energy relative to the conduction threshold, in poor agreement with both our calculation and with experiment). It is interesting to note that even a simple free-ion model using the observed $F^{-}(2s)$ ionization potential $(24 \text{ eV})^{69,70}$ and the point-ion field at the F site (12.45 eV) yields a reasonable result for the $F^{-}(2s)$ ionization limit in the solid (36.4 eV compared with the \triangle SCF result 37.2 eV and the observed value 37.6 eV).

The $F^{-}(1s)$ ionization limit is calculated to be at 694.2 eV (observed: 693.2 eV) and the interband spectra for this state are expected to start at about 708 eV. As seen from Table V, the band-structure and $\triangle SCF$ results for these transition energies differ by about 37 eV. Interestingly, while the $\alpha = 1$ exchange band model shows a somewhat better agreement with the observed transition energies than does the $\alpha = \frac{2}{3}$ exchange and correlation band model, it leads to much poorer agreement in the final $\triangle SCF$ limit [i.e., 720.1 eV compared with 694.5 eV for the $F^{-}(1s)$ ionization energy and 74.7 eV compared with 63.5 eV for the Li⁺(1s) ionization energy for $\alpha = 1$ and $\frac{2}{3}$, respectively]. The fact that the choice of $\alpha = 1$ yields larger eigenvalue separations in the band limit (and hence better agreement with experiment), has led many workers to favor this

value.^{16,17} It is gratifying that when a proper $\triangle SCF$ treatment is done, the results of the more correct choice of $\alpha = \frac{2}{3}$ are in much better agreement with experiment than those obtained with the artificial choice of $\alpha = 1$.

C. $F^{-}(2p)$ excitations

Our exciton model calculations for the optical region yield a $F^{-}(2p)$ -Li⁺(2s) exciton at 11.7 eV with a series limit at 13.9 eV. These compare reasonably well with the observed n=1 exciton at 12.6 ± 0.2 eV and the band gap at 14.2 ± 0.2 eV. To study the charge redistribution effects introduced by a valence hole, we again calculate the difference between excited and ground-state charge densities. Figure 11 shows the change in orbital density upon forming a 2p hole in the F⁻ free ion. The main effect is again a substantial contraction of the 2pshell, with smaller effects on the 2s density (the change in the 1s density upon forming a 2p hole was found to be negligible). The curve marked $\Delta \rho^{ion}(\mathbf{r})$ in Fig. 12 shows the total charge density change in a free ion due to formation of a p hole in a single F⁻site{i.e., $[5\rho(F^0, 2p^5) - 6\rho(F^-, 2p^6)] + 2[\rho(F^0, 2s)]$ $-\rho(F^{-}, 2s)$]. It is seen that this hole density has a considerable range and a nonvanishing magnitude even at the position of the nearest-neighbor F-. When the perturbed F^0 atom is placed in the solid, the resulting hole density $[\Delta \rho_{\rm NSC}^{\rm cry}(\vec{r})$ in Fig. 12] is slightly flattened but remains essentially similar to the free-ion hole density. However, upon iterating the solution to self-consistency, one obtains



FIG. 11. Orbital density differences in the F^- shells induced by a F 2p hole, as obtained in two independent SC calculations. The full dots indicate the positions of the ions in the solid.



FIG. 12. Total charge density difference due to a F 2p hole. $\Delta \rho_{NSC}^{cry}(r)$ and $\Delta \rho_{SC}^{cry}(r)$ denote the results obtained in the non-SC and SC limits, respectively, while $\Delta \rho^{ion}(r)$ indicates the corresponding hole density obtained for the free ion.

a charge density difference $[\Delta \rho_{sc}^{ay}(\mathbf{r})]$ in Fig. 12, in which we include only the density originating from the perturbed F site] that is dramatically shallower than the initial hole density. This final hole density is found to have a rather long tail and a nonexponential decay rate at distances larger than 4 a.u. from the perturbed site. It is hence clear that a valence hole in LiF is partially screened by the crystal electrons and differs considerably from a 2p hole in the free ion. Nevertheless, the localized hole density (up to a distance of 3 a.u. from the F^{0} site) is sufficient to shift the valence band edge to 14.3 eV below the vacuum limit (compared with 10.2 and 11.7 eV obtained from the band structure with $\alpha = \frac{2}{3}$ and 1, respectively) and to give rise to a bound exciton at 11.7 eV above the valence edge with a binding energy of 2.2 eV. The valence hole state in LiF is hence an intermediate case in that it cannot be described by either a free-ion model or a pure band approach.¹⁰⁹

Although our calculation was confined to a single $F^{-}(2p)-Li^{+}(2s)$ exciton state, the result obtained for the $F^{-}(2p)$ ionization limit in the crystal (14.3 eV relative to the point-ion corrected free-ion value of

15.9 eV) indicates that the exciton series would converge to the bottom of the conduction band (calculated value 13.9 eV), in agreement with the observation of Piacentini et al.⁷¹ but in conflict with the calculation of Kunz et al.⁸⁶ suggesting a series limit at the L gap (17 eV). Our calculated exciton binding energy of 2.2 eV agrees with the results of Piacentini⁷¹ (2.09 eV, obtained by fitting the observed data to a Rydberg series including central cell corrections) and with the calculated value of Collins et al.⁸⁵ (1.8 eV) obtained from a Slater-Koster one-band one-site impurity model. We note, however, that our result for the $F^{-}(2p)$ exciton contains some uncertainties due to a finite exciton-exciton interaction present in our superlattice model. The exciton transition energy obtained with the 8-atom unit cell (exciton-exciton distance of one nearest-neighbor) was 11.98 eV compared with 11.71 eV obtained with the 16-atom unit cell (exciton-exciton distance of $\sqrt{2}a$). To estimate the residual exciton-exciton interaction in the 16-atom unit cell calculation we have calculated the dispersion of the corresponding exciton band: the results for the exciton position at $\kappa = (0, 0, 0)$

and $\vec{\kappa} = (1, 0, 0)$ differ by 0.13 eV, indicating that residual interaction is still present in our superlattice model. This is undoubtedly caused by the extended tail of the valence hole density (compare Fig. 12) and can be treated by significantly enlarging the supercell's size. This demonstrates the inherent difficulty in describing such a perturbed crystal state (intermediate between a core exciton and a Bloch band) which has a pronounced charge localization near the perturbed site but a nonvanishing tail in its exterior part. A single-site localized impurity model⁸⁵ would hence seem inadequate for its treatment due to the slow decay of the perturbed density, while an effective-mass model would similarly mistreat the short-range localization effects.

It has been customary to assume⁸⁵⁻⁸⁶ that only the Coulomb electron-hole interaction is responsible for the exciton binding energy. To test this assumption we have estimated the contribution of the exchange and correlation energy to the exciton binding by calculating this energy directly from the self-consistent charge density difference (in the presence and absence of the exciton). The result showed that 0.51 eV (about 20% of the binding) is contributed by exchange-correlation interactions. This is a direct result of the substantial charge redistribution effects introduced by the exciton state which acts to localize the charge near the perturbed sites and hence to enhance the exchangecorrelation stabilization over that produced by a delocalized Bloch state.

Finally, we comment on the exciton band in the solid. Clearly, our treatment has not considered the translational degeneracy of excitons localized in different unit cells. When suitable exciton Bloch functions are formed from the single-site excitation functions¹¹⁰ and the crystal Hamiltonian is diagonalized in this representation, an exciton band results. In standard treatments of this effect one used either a Wannier model¹¹¹ appropriate for large radius excitons or a tight-binding Frenkel model¹¹² with the excited orbitals of the noninteracting subsystems used as zero-order trial wave functions. From our results, it seems obvious that the low members of the exciton series originating from a valence hole in LiF are not amenable to description by either of these limiting forms. We hence suggest that the SC relaxed wave func*tions* obtained in our crystalline \triangle SCF model be used as trial vectors for a more complete description of the exciton bands in these materials. Although a complete calculation of such an exciton band is outside the scope of the present study, we can compare relatively easily the width of such a band using our crystalline Bloch functions obtained from the self-consistent \triangle SCF model. Such a calculation shows a width of 0.3 eV for the $F^{-}(2p)$ exciton band in LiF [compared with a width of 0.01 eV similarly obtained for the $Li^{+}(1s) s$ -type exciton band]. Clearly, the valence excitons in LiF exhibit sizable interactions (cf., the range of the corresponding hole states in Fig. 12) that should be amenable to experimental observation.

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- ³⁷The results of Ref. 29 were later corrected for some errors in the zero-k-vector Fourier potential component and the diagonalization procedure used (cf., Ref. 30). The final results (corrected also for the eigenvector normalization error which occurred in Ref. 29)

were communicated to us by Dr. J. Fry for which we are grateful.

- ³⁸We have computed the Fourier coefficients of the exchange potential from our SC minimal-basis-set results and compared them with those obtained by Brener (Ref. 30) and Drost and Fry (Ref. 29) using their spherical averaging procedure. The comparison showed that their coefficients are much higher than ours for the first 3 reciprocal-lattice vectors. This has the effect of artificially scaling the exchange (i.e., using a highly
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$$\frac{F_{\pm}^{\text{corr}}(K)}{F_{\pm}^{\text{obs}}(K)} = \frac{(f_{\text{F}} \pm f_{\text{Li}})}{(f_{\text{F}}e^{-B_{\text{F}}[(\sin\theta)/\lambda]} \pm f_{\text{Li}}e^{-B_{\text{Li}}[(\sin\theta)/\lambda]})},$$

where the Debye-Waller factors $B_{\rm F}$ and $B_{\rm Li}$ were taken from Ref. 47. Note that this procedure assumes a superposition model for the crystal density and is hence not unique. We are grateful to Dr. R. N. Euwema for a discussion of this procedure.

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- 109 Fowler (Ref. 108) suggested that the band gaps obtained in LDF band models be corrected for long-range correlation effects (in the semiclassical limit) before comparison with experiment is made. Hence the bandstructure results for the gaps in solid Ar and KCl (13.3 and 6.4 eV) were corrected by the Mott-Littleton terms (-2.0 and -3.4 eV) and yielded results which are much too small relative to the experimental data (14.3 and $8.9\ {\rm eV},\ {\rm compared}\ {\rm with}\ {\rm the}\ {\rm calculated}\ {\rm results}\ {\rm of}\ 11.3$ and 3.0 eV for Ar and KCl, respectively). It was hence suggested that these discrepancies are caused by some defects in the exchange used in the band models. This analysis completely overlooks the presence of the screened self-interaction terms in the LDF theory which are positive and usually much larger than the self-energy correlation terms. Any localization of the electron or hole states in these narrow band materials (cf. Fig. 12) would then switch on these self-interaction Π_{II}^0 terms and cause a substantial *increase* in the

computed band gap. We indeed find that this is the case in the LiF crystal (cf. Table V) and suspect that this might also be the case in other narrow-band materials like rare-gas crystals. On the other hand, the computed Hartree-Fock one-electron energy gaps are usually much larger than the observed ones (e.g.,

 $18.5\ \text{eV}$ for Ar and $23.1\ \text{eV}$ for KCl) and self-energy terms that tend to reduce these values are indeed the only relevant corrections.

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