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Calculated properties of a prototypical ionic monolayer

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First-principles predictions are made of the ground-state behavior of the simplest realistic ionically bound ultrathin film, a LiF monolayer, in particular, the structure, energetic properties, charge distribution, charge transfer, and proton stopping. All-electron, full-potential, local-density functional methodology was used. Fifteen basis sets plus variants were tested in order to insure meaningful results. The internuclear distance, total energy, and band structure (Kohn-Sham eigenvalues) all stabilize with respect to basis-set size at moderate levels (Li: $9s4p$; F: $10s7p+1p_z$, both contracted). The equilibrium internuclear distance of the LiF-$1L$ is predicted to be 3.50 a.u., smaller than the calculated (experimental) bond distance for the crystal, 3.86 a.u. (3.80 a.u.). The charge distribution is quite flattened into the nuclear plane relative to the crystal. This combination (shortened bond and flattened charge distribution) may be significant for epitaxial growth. Also in contrast with the crystal, the monolayer has an indirect gap. As would be expected, most of the binding is in the molecular bond, a fact which makes proton stopping for the monolayer only slightly different from that for the molecule. This behavior confirms the Bragg rule relative to the diatomic molecule, and hence violates that rule relative to the separated atoms.

I. INTRODUCTION

Alkali halides such as LiF long have been considered the prototypes of ionically bound systems, with the strength of the ionic binding mechanism having made their structure and properties a topic of interest since at least the first decade of this century.[1] However, no comprehensive treatment of the extreme limiting case of an alkali halide ultrathin film, a monolayer ("$1L$" hereafter), has ever appeared, to our knowledge. That limiting case is important for at least two reasons. Systematic knowledge of the $1L$ provides, first of all, an interpretation of existing information about the bulk crystal for the cases of decreasing thickness with which real samples can be made by modern techniques. Equally important, it is reasonable to suspect that large effects on bond lengths, charge densities, and one-electron excitation energies would result from the combination of extremely strong ionic binding and the peculiar planar coordination of the $1L$. This study shows such speculation to be well founded.

Some background is appropriate given the venerability of study of alkali halides. Quantum mechanical calculations of one-electron energies in LiF crystals apparently were attempted first by Ewing and Seitz.[2] They concluded that, contrary to canonical notions, the binding was a combination of predominantly metallic and covalent mechanisms. However, Yamashita's tight-binding calculation[3] produced a cohesive energy, compressibility, and lattice constant all in good agreement with experiment. Such tight-binding behavior certainly is consistent with bonding dominated by ionicity. Twenty years after Ewing and Seitz, Löwdin treated several alkali halides, including LiF, via a formulation of linear combination of atomic orbitals (LCAO) methodology for the Hartree-Fock (HF) problem which included techniques still in use but with a focus on elastic constants.[4] Again the results were consistent with conventional ionic binding concepts.

Ten years later, Mansikka and Bystrand[5] also seemed to confirm the ionic nature of the binding in their Heitler-London calculation based on free-ion spin orbitals scaled variationally so as to retain satisfaction of the virial theorem. Unsurprisingly, the late 1960s and most of the 1970s produced a considerable number of treatments of LiF,[6-16] in both the local-density approximation (LDA) to density-functional theory (DFT) and in the HF approximation. Most were focused on energy bands but the most recent, Zunger and Freeman (Ref. 12, ZF hereafter), provides a full LDA calculation of ground-state crystalline properties. References 14–16 provide a similar comparison with crystalline HF calculations.

On the molecular side there are several calculations on the LiF monomer (citations to much of the earlier work are in Ref. 17), but only three seem to have treated the planar oligomers [$(\mathrm{LiF})_n$, $n=2,3,4$] with full quantum-mechanical optimization (within the HF approximation) of the geometry.[18-20] We are not aware of any other first-principles calculations of planar LiF clusters.

It appears that only one detailed treatment of any ordered, nominally ionic $1L$ has been published, namely, the small-basis HF calculation of the LiH $1L-5L$ sequence by Causa, Dovesi, and Ricci.[21] The same authors did a similar small-basis HF calculation of the LiF $3L$ in the HF approximation.[22] No LDA treatment of an alkali halide $1L$ has appeared.

Various of us have calculated the properties of ordered

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covalently, molecularly, and metallically bonded films.[23–25] In addition to addressing the issues listed at the outset, this study also completes the coverage of bonding mechanisms in ordered 1*L*'s. Of particular interest is the extent to which the 1*L* configuration modifies the system behavior (relative to the counterpart crystal) in the context of the strong binding provided by the ionic mechanism.

In order, the following sections consider basis-set selection (including possible basis-set effects on calculated charge transfer) and other technical issues, ground-state properties, one-electron band structure (Kohn-Sham eigenvalues) and charge transfer, and proton stopping at equilibrium. A brief summary of the most important findings and comments on their potential implications concludes the text.

II. TECHNICAL MATTERS

With the exception of CsCl, CsBr, and CsI, the alkali halides assume the rocksalt (NaCl) structure under normal conditions, hence display an octahedral distribution of either ion type with respect to the other. The symmetry of the (100) planes is therefore the obvious one to study for a LiF 1*L*. Figure 1 shows the lattice and primitive unit cell: the Li-F internuclear distance *R* is the key structural parameter.

As in our previous work, self-consistent, all-electron, full-potential calculations were performed in the local density approximation to density functional theory. The primary LDA model utilized was that of Hedin and Lundqvist, but for comparison with other work some $X\alpha$ calculations were performed also.

FILMS, the code package developed by two of us[24] for treating ordered ultrathin films of arbitrary symmetry, composition, and thickness, solves the Kohn-Sham equation via linear combinations of Gaussian-type orbitals and fitting functions.[26] The Kohn-Sham orbitals are expanded in a basis of Gaussian-type functions (the "KS basis"), while both the charge density $n(\mathbf{r})$ and the LDA exchange correlation kernels which depend nonlinearly upon n are expanded in auxiliary Gaussian-type bases (the "*Q* basis" for fitting n and the "XC basis" for fitting the exchange-correlation kernels). The *Q* basis coefficients are obtained by minimization of the residual Coulomb repulsion caused by the difference between the exact and fitted densities, while the XC fitting is by least squares on a numerical grid (in essence, a numerical integral in two stages). Although formulated with distinct *Q* and XC basis sets, experience has shown it usually to be better to use a single, common fitting basis (elsewhere the common fitting basis is labeled as the "*F*" basis, but to avoid confusion with the chemical symbol *F*, "QXC" is used here).

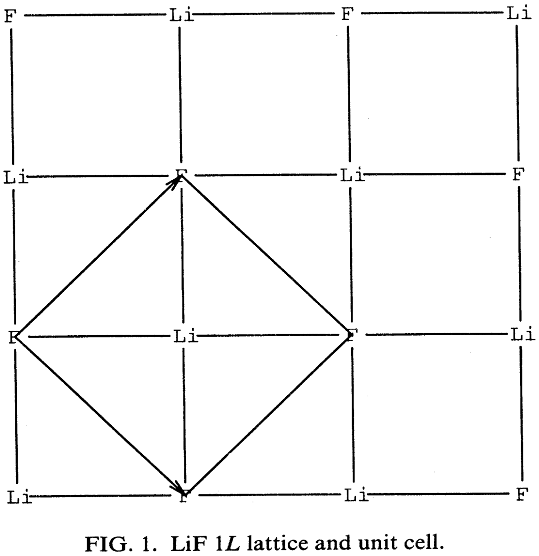

FIG. 1. LiF 1*L* lattice and unit cell.

Textbook-pure ionic binding (unit charge transfer for LiF) would correspond to closed shells and localized electronic distributions with approximately spherical symmetry at each nuclear site. A calculation such as this one is challenged from the outset, therefore, to avoid basis-set choices which are biased with respect to that elementary chemical picture.

Qualitatively, both nominally ionic or nominally atomic KS basis sets would seem to be acceptable. To construct an ioniclike KS basis from a standard tabulation for *F* (e.g. van Duijneveldt,[27(a)]), we typically added one or more diffuse functions to the *p*-type basis [cf., e.g., Ref. 27(c)]. For Li, it was more appropriate to begin with the Li 1*L* basis used in Ref. 24, then delete one or more of the most diffuse *s*-type functions (because of the shift away from the metallic character of the Li 1*L*). These alterations correspond quite literally to accounting for the diffuseness of anions and compactness of cations relative to their neutral antecedents. The atomiclike KS basis sets were obtained from tabulated sets by removing (and/or tightening) only those more diffuse *s*-type functions which caused approximate linear dependencies in the film. Usually this procedure resulted in a Li basis with substantial overlap at the F sites in the 1*L*, whereas the F basis was somewhat less diffuse. Nominally atomic, this choice is also equivalent to charge transfer, consistent with the observation by Chaney *et al.*[8] that the Li 2*s* function overlaps the F atoms, while the F 2*s* and 2*p* orbitals are less diffuse and overlap the Li sites much less strongly. Of course a few Li *p*-type functions are necessary for bonding in either kind of KS basis set.[27(b),27(c)] Contractions were restricted to the very localized *s*-type functions and to F *p*-type functions with coefficients from van Duijneveldt[27(a)] in all cases.

Fifteen KS basis sets, both atomiclike and ioniclike, were explored. Perhaps counter intuitively, all the ioniclike sets could be discarded on grounds of high total energies, instability of the calculated magnitude of the KS band gap with respect to small changes in the basis set, and peculiar ordering of the occupied KS states. Testing of the atomic basis sets showed that at least $8s2p$ for Li and $11s6p$ for F (before contraction) was required to achieve stability of the calculated equilibrium *R* (denoted as R_e hereafter) to about ±0.02 a.u. and of the calculated E_{tot} per ion pair to about ±0.005 hartree. However, a basis set of this size was *not* rich enough to achieve a stable calculation of the KS band gap. This outcome is unsurprising, since the KS band gap is not a variationally stabilized quantity. Stability of the calculated band gap required a primitive $12s4p$ Li basis contracted to $9s4p$ and a primitive F $13s8p1p_z$ basis contracted to $10s7p1p_z$. Note that the single additional diffuse p_z function is a small but important contributor to a stable representation. The resulting basis is shown in Table I.

Testing also showed that a QXC basis with exponents found by doubling the exponents of the KS basis is a reliable, convenient choice for this system. Obvious exceptions (signaled by very small relative contributions to the Q expansion) were the two tightest d-type functions on the F sites and the two tightest s-type functions on the Li sites. In both cases these were replaced with a single compromise value which had no discernible effect on the outcome; see Table I.

This return to the "Dunlap rule"[28] for forming the QXC basis is of some technical interest, since other systems (see Ref. 24) have been described best by a QXC basis essentially identical with the KS basis. Almost all those other systems were metallic, however, hence required a relatively diffusive QXC basis to represent the substantial interstitial and exterior electron densities satisfactorily. The high degree of charge localization associated with LiF ionic binding (e.g., less than 10% of the electrons per cell are in the interstitial and exterior regions at the calculated R_e, for any reasonable definition of interstitial and vacuum) manifestly corresponds to the appropriateness of a much more localized QXC basis than would occur if the KS basis were to be used.

Although the eventual test of basis-set adequacy must be (and was) the stability of calculated results against basis-set changes, there are other useful metrics. In particular, for Q fitting the parameter

$$\lambda=\int d^3r\int d^3r'\frac{n_n(\mathbf{r})[n(\mathbf{r}')-\tilde{n}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}$$

[where $n_n(\mathbf{r})$, $n(\mathbf{r})$, and $\tilde{n}(\mathbf{r})$ are the nuclear number density, neutralized electron number density, i.e., electron density neutralized cell-by-cell by the nuclear array, and fitted neutralized electron number density, respectively] is a nuclear-density-weighted average of the quality of fit.[26] Typically $\lambda<5\times10^{-8}$ hartree near the calculated R_e. As usual, one must check that the magnitude of any spurious negative charge (from the Q fitting) is quite small in absolute value throughout the unit cell; in fact it was zero to available numerical precision in a substantial neighborhood of the calculated R_e. By testing for the onset of significant approximate linear dependencies and/or negative electron densities, the range of R over which the QXC basis is valid also can be determined. The effective range in R of this QXC basis is from 3.25 to 4.3 a.u., as determined by the onset of negative density with absolute value $>10^{-5}$.

Finally, to sample the irreducible wedge of the two-dimensional Brillouin zone, we used a 10 **k** point grid in the two-dimensional analog of the linear analytic tetrahedral scheme familiar in crystalline calculations for BZ integral evaluation.

TABLE I. KS and QXC basis exponents. The first four s-type functions for both Li and F and the first two p-type for F are contracted, each into a single function. The contraction coefficients are in parentheses. These bases are constructed from the $13s8p$ atomic F and $13s$ atomic Li sets tabulated by van Duijneveldt (Ref. 27).

KS	QXC
Fluorine	
s-type	
103 109.46 (0.000 064)	
15 281.0070 (0.005 03)	s-type
3 441.5392 (0.002 668)	206 218.920
967.094 83 (0.011 200)	30 562.0140
	6 883.078 40
314.035 34	1 934.189 70
113.442 30	628.070 680
44.644 727	226.884 600
18.942 874	89.289 454 0
8.532 7430	37.885 748 0
3.919 4010	17.065 486 0
1.568 1570	7.838 802 00
0.623 2900	3.136 314 00
0.2408 610	1.246 580 00
	0.481 722 00
p-type	
245.330 290 (0.000 985)	d-type
56.919 005 0 (0.008 257)	153.838 010
	35.209 136 0
17.604 568 0	12.549 990 0
6.274 995 00	4.894 060 0
2.447 030 0	1.990 120 0
0.995 060 0	0.807 946 0
0.403 973 00	0.309 620 0
0.154 810 0	
p_z-type	
0.050 00	
Lithium	
s-type	
9497.934 40 (0.000 075)	s-type
1416.811 200 (0.000 584)	3233.622 40
321.459 940 (0.003 062)	642.919 880
91.124 163 0 (0.012 605)	182.248 330
	59.999 782 0
29.999 891	22.035 262 0
11.017 631 0	8.745 602 0
4.372 801 0	3.662 512 0
1.831 256 00	1.604 522 0
0.802 261 00	0.725 296 0
0.362 648 00	0.227 990 0
0.113 995 00	0.102 474 0
0.051 237 00	
	d-type
p-type	5.120 00
2.560 00	3.760 00
1.880 00	0.720 0
0.360 0	0.272 0
0.136 0	

III. GROUND-STATE STRUCTURE AND ENERGETICS

Calculated equilibrium quantities are summarized in Table II while Fig. 2 shows $E_{\mathrm{tot}}(R)$. Note that the infinite R limit of this curve corresponds to separated F^- and Li^+ ions with the unphysical *common* Fermi energy enforced upon heteronuclear systems by the LDA.[29]

Monolayer equilibrium corresponds to $R=R_e=3.50$ a.u. Table III shows that this value is roughly midway between the molecular and crystalline values, consistent with the "coordination model" discussed in Refs. 24 and 30–32. There is one exception to the steady increase of bond length with increasing aggregation, namely the finding in Ref. 17 (without comment) that R_e for the cyclic dimer $[(\mathrm{LiF})_2]$ is slightly larger than for the cyclic trimer. Reference 17 also shows that there is significant influence of the molecular conformation upon R_e. Specifically the linear trimer exhibits a range of values from 3.04 to 3.21 a.u. depending on which Li—F bond was examined. Presumably the anomalous contraction in going from the cyclic dimer to cyclic trimer is another example of such small system behavior, hence is not particularly relevant to the 1L.

The two crystalline calculations of R_e which are apparently the most reliable (the "basis set II" LDA results from ZF and the Hartree-Fock calculation of Ref. 14) bracket the measured value, 3.80 a.u., almost symmetrically by about 0.05 a.u. The HF and LDA treatments of the isolated monomer also give very similar values of R_e. Given the major differences between the two theoretical models, this near agreement is striking. It suggests, strongly, that the present 1L results can be compared with those from the crystal without the caution usually needed to avoid spurious predictions caused by LDA lattice contraction (for details, see Ref. 31). Compared with experiment, therefore, the LiF 1L is bond-contracted by 7.9%. This is just what would be expected qualitatively from the coordination number model, though the predicted percentage decrease is among the largest of which we are aware.

For an ionically bound molecular system there are three obvious possible definitions of the cohesive energy. One is the energy per pair relative to individual, isolated free atoms. The only experimental value for crystalline LiF seems to be that quoted long ago by Seitz[33] for $T=300$ K, namely, -0.345 hartree/pair ($=-9.39$ eV/pair). In the HL LSDA, the total energies of the free Li and F atoms from $13s$ and $13s8p$ basis sets, respectively, are $-7.354\,51$ hartree (Li) and $-99.118\,71$ hartree (F, spin polarized). The 1L cohesive energy with respect to this reference is -0.3419 hartree/pair ($=-9.30$ eV/pair).

A somewhat more usual definition for diatomic ionic crystals (but less accessible for a LDA calculation; see below) is the energy per pair relative to the isolated constituent ions. The experimental cohesive energy for crystalline LiF in this case is -0.395 hartree/pair ($=-10.75$ eV/pair) at $T=0$ K.[34] ZF quote the observed E_B for crystalline LiF, corrected for zero point energy by use of the Debye formula, as -10.6 eV/pair and calculate a value of -9.8 ± 0.5 eV/pair at the calculated R_e. Two issues arise in interpreting this result. ZF used the Singwi *et al.* LDA,[35] not the HL form used here. Secondly, because of improper self-interaction cancellation, no LDA (to our knowledge) can yield a properly bound negative ion without introduction of some arbitrary confining potential.[36,37] ZF did not specify their choice of confinement potential but it is clear from the paper that they cite (regarding calculation of free ion energies "by standard methods") that such a potential was used. Unfortunately ZF published neither the free ion nor crystalline total energies which they obtained.

The fundamental difficulty with anions in the LDA when combined with ZF's omission of total energies makes it difficult to calculate a proper 1L binding energy relative to separated ions. An attempt to circumvent the problem by appeal to experimental values for the ionization energy of Li (5.390 eV $=0.198\,08$ hartree, Ref. 38) and the electron affinity of F (-3.40 eV$=-0.1249$ hartree) (Ref. 39) unfortunately fails. That is, if one adds these quantities to the LDA total energies for the neutral atoms, the result is a total energy for the free F^- plus the free Li^+ of -106.4000 hartree. This in turn yields a 1L E_B with respect to free ions of 0.4150 hartree/pair $=$ 11.29 eV/pair, or a prediction that the 1L is more bound than the crystal, a clearly unrealistic result which invalidates the attempted estimation of the ionic energies. This is yet another example of the general problem of cohesive energies as small differences between large numbers, the computation of which must be done on an equal footing. The attempted estimate, a mixture of experimental and computed values, clearly does not meet that requirement.

The third choice of binding energy definition is to recognize that most of the binding in an extended LiF system (be it crystalline or film) is already present in the isolated molecule, hence the 1L binding should be referenced to the molecule. We prefer this choice on two grounds. Chemically the LiF molecule is the interesting constituent. Technically the problem of LDA mistreatment of a free negative ion is eliminated.

Neyman and Rösch[40] have found the molecular R_e as 2.974 a.u. and $E_{\mathrm{tot}}=-105.873\,05$ hartree from the $X\alpha$ LDA (with $\alpha=\frac{2}{3}$). The corresponding spin-polarized

TABLE II. Optimized ground-state quantities: R_e is the equilibrium Li—F bond length, E_{tot} the total energy per unit cell, E_g the band gap (indirect), W the valence bandwidth, and TVB the top of the valence band relative to the vacuum.

Reference atomic bases		Monolayer bases		R_e	E_{tot}/(ion pair)	E_g	W	TVB
F	Li	F	Li	(a.u.)	(hartree)	(eV)	(eV)	(eV)
$13s8p$	$13s$	$13s8p1p_z/10s7p1p_z$	$(12s4p)/[9s4p]$	3.50	$-106.815\,08$	6.83	2.74	-7.77

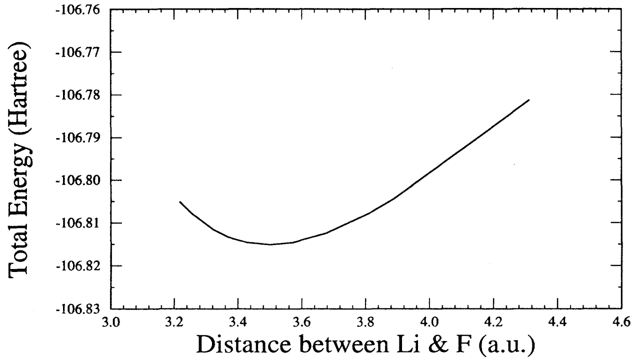

FIG. 2. Total energy per ion pair vs internuclear distance for the LiF 1L.

atomic energies are -7.19338 hartree (Li) and -98.47333 hartree (F), so that LDA finds the isolated LiF molecule to be bound by 0.206 hartree $=5.61$ eV.[42] We find the LiF 1L $X\alpha$ minimum E_{tot} to be 105.969 36 hartree/pair, or a 1L bound by 0.096 hartree/pair ($=2.61$ eV/pair) with respect to the free molecule.

Note that Neyman and Rösch could use a somewhat richer basis than ours,[27(b),27(c)] for example, d-type KS functions. Careful calibration of the two calculations was desirable therefore. The test chosen was to optimize R using the $X\alpha$ LDA ($\alpha=2/3$) for a very expanded square LiF 1L, with edge length 15.0 a.u. and the LiF molecule aligned along the x-axis edge. In this case p_x-type QXC functions are essential. Beginning with the exponents proposed by Jörg *et al.*[27(c)] (3.906 25, 1.5625, 0.625, 0.25, 0.1), the most diffuse two for F and the most diffuse three for Li were removed in order to get a QXC basis stable over a reasonable range of R values. The expanded 1L yields an estimate of the molecular $X\alpha$ $E_{\text{tot}}=-105.87506$ hartree/pair compared with -105.87305 hartree/pair from Neyman and Rösch.[40] The R_e comparison is 2.94 a.u. for the expanded 1L compared to 2.974 a.u. calculated for the isolated molecule.[41] Clearly there is a small amount of residual lattice binding (0.05 eV/pair) still present in the expanded 1L. Since the two calculations use completely separate codes and treat systems that are not literally equivalent, the near agreement of both E_{tot} and R_e validates the use of the Neyman-Rösch molecular results.

IV. ONE-ELECTRON PROPERTIES AND CHARGE TRANSFER

To treat charge transfer it is helpful to start with the conventional energy bands (bare Kohn-Sham one-electron energies); see Fig. 3. The lowest bands, the F and Li 1s-like ones, are omitted since they are sensibly flat. At Γ they lie at -24.010 and -1.754 hartree, respectively. The next higher occupied band (the lowest shown in Fig. 3) is dominated by F 2s but with Li hybridization.

The highest occupied bands are predominantly F 2p-like though again with significant Li admixture. The two-dimensional symmetry of the 1L is manifest in the doubly degenerate even-symmetry (with respect to the 1L plane) p_{xy} state at Γ which lies slightly above a singly degenerate odd symmetry p_z state. In contrast, these merge in the LiF crystal to form the triply degenerate Γ_{15} level (compare, for example, Fig. 2 of ZF). The dominance of ionic bonding over system geometry is indicated by the width of this 1L band, about 2.74 eV as compared with calculated crystalline values of 2.31 eV from ZF (for $X\alpha$ LDA with $\alpha=1$), 3.12 eV by Lobatch *et al.*[42] (who used the HL LDA), and 3.1 eV from HF.[16] That is, substantial charge transfer broadens this band to essentially its full calculated crystalline width at only one layer even though the symmetry-induced splitting is quite different in the two systems. This result is consistent with the shortened 1L bond length relative to the crystal.

The 1L calculation sheds relatively little light on the long-noted smallness of the calculated valence bandwidth relative to experiment, as might be expected. Discussion and citations of experimental literature are in Ref. 16. Perhaps the problem is simply one of inappropriate use of bare KS bands, but this seems unlikely since the HF value is in the same neighborhood. It is interesting and perhaps suggestive that the experimental valence bandwidth for LiF(100) deposited epitaxially on Ge(100) is 3.5 eV,[43] much smaller than the 4.5–6-eV values reported experimentally for the LiF crystal and much closer to the range of calculated results.

For the 1L the lowest conduction band is the s-like hybrid just as in the crystal.[12] The 1L differs significantly from the crystal in having an *indirect* gap, from J to Γ, of 6.83 eV. The 1L direct gap at Γ is more than 0.4 eV larger, 7.26 eV. As usual in insulators, the KS eigenval-

TABLE III. Comparison of various LiF equilibrium bond lengths.

System	R_e (a.u.)	Method; Source
isolated monomer	2.94, 2.97	Hartree-Fock, CI(SD); Ref. 17
isolated monomer	2.974	LDA ($X\alpha$, $\alpha=\frac{2}{3}$); Ref. 40
isolated cyclic dimer	3.27, 3.23	Hartree-Fock; Refs. 19, 20
isolated cyclic trimer, quadramer	3.23	Hartree-Fock; Ref. 20
monolayer	3.50	This calculation
crystal	3.87	LDA (Singwi *et al.*); Ref. 12
crystal	3.75	Hartree-Fock; Ref. 14
crystal	3.80	Experiment; see Ref. 12

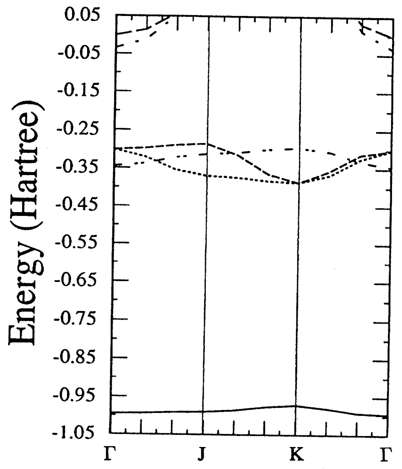

FIG. 3. Kohn-Sham band structure for the LiF $1L$.

ues underestimate the band gap[44] because of the omitted derivative discontinuity contribution.[45] This well-documented defect in the use of bare KS bands appears in the crystalline results, for which experimental values of 13.6 eV (Ref. 46) and 14.2 eV (Ref. 47) have been reported, compared with ZF's calculated 9.8 eV ($X\alpha$, $\alpha=\frac{2}{3}$), 10.5 eV ($\alpha=1$), and 9.9 eV (Singwi *et al.* LDA, Ref. 35). Assuming a consistent 30% bare KS gap underestimate for the $1L$, the present calculation predicts that the measured $1L$ indirect gap would be about 9.8 eV and the direct gap about 10.4 eV.

The $1L$ Li $1s$ core state lies 46.8 eV below the bottom of the conduction band, whereas experimentally the Li$^+$ K-shell x-ray absorption spectrum structure begins at 60 eV.[48] Scaling the calculated value by the same amount (30%) as the bare KS band gap gives 60.8 eV. However, there may be some $1L$ versus thick-film effects involved as well. Film thicknesses were not reported in Ref. 48(b) and not measured in Ref. 48(a), but clearly they were large compared to the $1L$.

Figure 4 displays the ground-state charge-density distribution in two ways. The minimum in the density along the Li-F axis, as seen in Fig. 4(b), is 61.1% of the distance from F, just as ZF found for crystalline LiF (61.6%) and, as well, in excellent agreement with the earlier calculation of Ref. 8. The comparison with the crystalline experimental value, 61.2%, is also excellent.[49] The magnitude of the density at the minimum, 0.033 $e/\text{a.u.}^3$, is larger than both the experimental crystalline value from Ref. 48, 0.022 $e/\text{a.u.}^3$, and ZF's calculated crystalline value, 0.023 $e/\text{a.u.}^3$

Those density shifts are consistent with the contracted bonds of the $1L$ relative to the crystal. At first inspection, in fact, most of these features are in line with the qualitative character of the charge distribution plot, Fig. 4(a), namely, ionic bonding is so strong that the in-plane charge density plot of the ordered $1L$ does not differ qualitatively from that of the corresponding crystalline plane. This assessment misses something important. A clue is the 50% larger density at the minimum just noted. Comparison of Fig. 4(b) with Fig. 6 of ZF shows that, at 25% of the bond distance from an F site, the $1L$ charge density is about 0.63 $e/\text{a.u.}^3$ while the density at the corresponding position in the crystal is only about 0.10 $e/\text{a.u.}^3$ Clearly part of the density from the z-direction bonds in the crystal goes into the x-y plane in the $1L$. The ionic bond is so strong that the charge distribution around each site in the $1L$ has a much lower aspect ratio than in the crystal: the $1L$ density distribution is more like a low, flat cylinder than the nearly spherical contours found in the crystal. The $1L$ bond contraction relative to the crystal is another manifestation of the same flattening of the charge density into the plane of the $1L$.

Traditional analysis of ionic bonding is in terms of charge transferred. For the isolated molecule, the charge transfer deduced from the measured electric dipole mo-

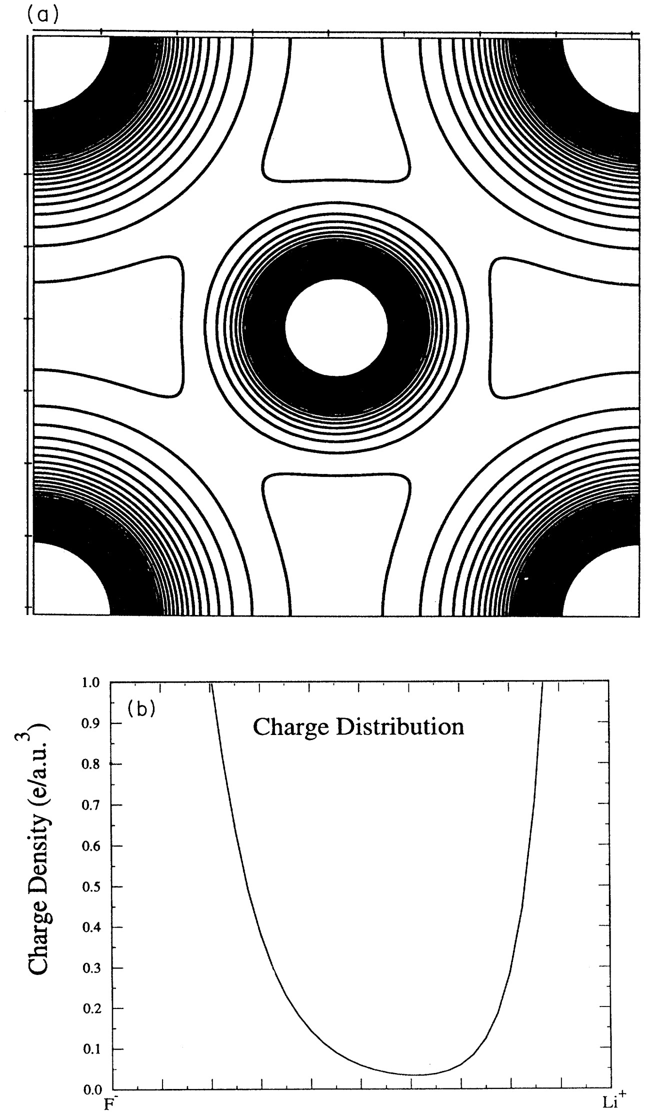

FIG. 4. (a) Contour plot of the in-plane ground-state charge distribution; Li site at center, F sites at corners. (b) Total ground-state charge-density distribution along the line joining the Li and F sites.

ment is given by Smith *et al.*[50] as 0.84 and by Pauling[51] as 0.91 (read from his Fig. 3-8). From Pauling's electronegativity scale[52] one gets 0.895, while the universal bonding model of Smith *et al.*[50] yields 0.84 and the simplified atomic LDA model of Kitamura *et al.*[53] gives 0.91. Apparently the only value extracted from crystalline data is from Phillips and Van Vechten,[54] who find 0.915.

ZF raised a serious cautionary note about the whole charge-transfer concept by performing a LCAO charge analysis with a Bloch basis orthogonalized at each sample point in the zone. They found the apparent ionicity to be quite different at Γ and X, 0.38 and 0.45, respectively, and very different from the charge-transfer values just quoted (which are reasonably close to the classical free-ion value).

Earlier Brener[11] had obtained rather similar results by a simpler procedure. He assumed spherical symmetry for the charge moved to F, then did a simple spherical-volume integral from the F ion out to the point where the change in the charge density (with respect to superposed atoms) went to zero. He found approximately 0.46 electron transferred.

Neyman and Rösch[40] found the dipole moment of the molecule to be $-2.289\,10$, $-2.808\,08$, and $-3.092\,14$ a.u. at the internuclear distances of 2.853, 3.458, and 3.798 a.u., respectively ($X\alpha$ LDA, $\alpha=\frac{2}{3}$). The corresponding charge-transfer values are 0.802, 0.812, and 0.814. The increase of charge transferred as the internuclear distance increases is similar to that found in the LiF $1L$ and may be related quite closely to the LDA separated atom problems first analyzed by Perdew and Smith.[29] They showed that, because the LDA imposes a common Fermi energy even when the F^- and Li^+ sites are separated greatly, there is a spurious nonvanishing asymptotic charge transfer which yields a spurious dipole moment of arbitrarily large magnitude.

In the face of all these ambiguities of defining and calculating charge-transfer values, we decided to use a simple, albeit arbitrary procedure (rather than expend effort on a more sophisticated but still arbitrary one). In the fitting function technique, the XC fitting step inevitably involves numerical integrals. The numerical mesh we use includes muffin-tin regions around each nuclear site. For the LiF-$1L$, we chose the muffin-tin radii to be determined by the location of the charge minimum along the Li-F axis [recall Fig. 4(b)], hence the radius at the F site was 61.07% of the internuclear distance, whereas for the Li site it was 38.93%. At the calculated R_e, the charges in the F and Li spheres are 9.259 45 and 2.000 66, respectively. On the assumption that the charge in the interstitial and vacuum regions defined by the numerical integration scheme is apportioned the same, the total charge transfer is 0.867 electrons. This value, which is close to the result from Feyman and Rösch, is consistent with the flattening, relative to the crystal, of the $1L$ charge distribution into the plane of the nuclei discussed above.

V. PROTON STOPPING

The stopping cross section per scatterer (here the electron distribution for an LiF ion pair) $S(\mathbf{v})$ for a charged particle of nonvanishing mass traversing a material system is

$$-\frac{1}{N}\frac{dE}{dx}=S(\mathbf{v}) ,$$

where N is the number density of scatterers, $\mathbf{v}$ is the velocity of the incident particle (normal incidence), E is its energy, and x is its path length. For a proton incident on a material, the electronic $S(\mathbf{v})$ is a measure of aggregate energy deposition into the electron population by the proton, and hence probes the one-electron energies and generalized oscillator strengths.[55]

While many stopping calculations have been performed in the last half century, none appears to have treated an ionically bound crystal or molecule, except by using Bragg's rule, i.e., the assumption that $S(\mathbf{v})$ for the compound is the linear superposition of the stopping for its components.[56] Bonding in LiF is so strong that superposition is of dubious validity on the face of it, however. Mean excitation energies have been calculated for crystalline LiF from the local plasma approximation (LPA; see below),[57] but the requisite electron densities $n(\mathbf{r})$ were estimated roughly from those of corresponding neutral atoms and from ionic bond parameters.

Only a few experimental results are available for energy deposition in condensed LiF. These include proton stopping data by Bader *et al.*[58] (now rather old), Kubo's proton depth profile results,[59] and stopping data for 1–2 MeV alphas by Biersack *et al.*[60]

We considered the electronic stopping power for a proton in both the LiF-$1L$ and in the dilute molecular gas limit. Electron capture by the proton (charge-state changes), and ionic dissociation of LiF were neglected. To incorporate the material properties of the target in the calculation realistically, it is essential to evaluate the mean electronic excitation energies on which the stopping cross sections depends in a state-dependent fashion.[61]

Direct calculation of generalized oscillator strength distributions for arbitrary momentum transfers is, at present, a prohibitive task even for light atoms.[55,62] Following Sabin and Oddershede therefore, we employed Sigmund's kinetic theory of stopping[63] in the form

$$S(\mathbf{v})=\frac{4\pi Z_1^2 Z_2}{v^2}L(\mathbf{v}) ,$$

where the stopping number is an orbital superposition $L(\mathbf{v})=\sum_l L_l(\mathbf{v})$ with each contribution given by the kinetic theory transformation

$$L_l(\mathbf{v})=\int d\mathbf{v}_2\rho_l(\mathbf{v}_2)L_l^0(|\mathbf{v}-\mathbf{v}_2|)\frac{\mathbf{v}\cdot(\mathbf{v}-\mathbf{v}_2)}{|\mathbf{v}-\mathbf{v}_2|^3}v .$$

Here Z_1 is the projectile charge, Z_2 is the number of electrons per molecule, and $\rho_l(\mathbf{v}_2)$ is the momentum density of the lth energy subband (see below).

The stopping number integrand L_l^0 is of Bethe form with a low-energy cutoff

$$L_l^0(v)=\frac{\eta_l}{N_c Z_2}\ln\left[\frac{2v^2}{I_l}\right]\theta\left[v^2-\frac{I_l}{2}\right] ,$$

where N_c is the number of molecules per unit cell and η_l is the norm of $\rho_l(\mathbf{v}_2)$. The orbital mean excitation energies I_l were calculated via the orbital local plasma approximation[64] (OLPA)

$$\ln I_l = \frac{1}{\eta_l}\int_{-\infty}^{\infty} dz \int_A d\sigma\, n_l(\mathbf{r}) \ln\{[4\pi n(\mathbf{r})]^{1/2}\}$$

with A the planar unit cell area and $n_l(\mathbf{r})$ the partial density for the lth energy subband (see below).

The momentum density in the kinetic theory expression was obtained by direct Fourier transform of the KS eigenfunctions. The Lam-Platzman correction,[65] which is small, was omitted. The atomic calculations used the same OLPA and LDA but were spin polarized in the central field approximation. Details are in the Appendix of Ref. 66.

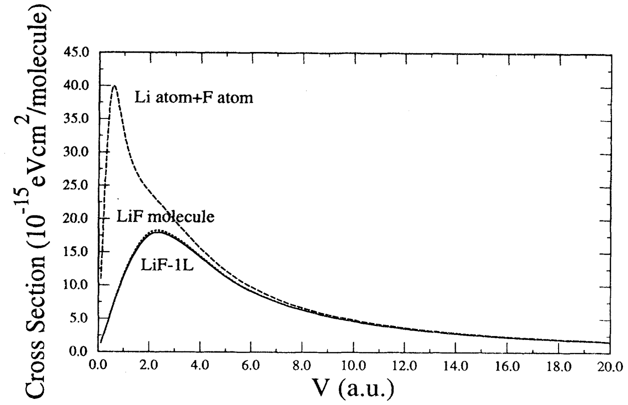

FIG. 5. Calculated stopping cross sections for the LiF-1*L*, LiF quasimolecule, and Bragg rule (Li atom+F atom). The units are 10^{-15} eV cm^2/molecule.

The OLPA grouping of levels is not as obvious for the periodic system as it is in the atomic case. In particular, the OLPA could be done by band (i.e., irreducible representation label and compatibility relations) or by energy interval (so-called "windows"). Windows turn out to be quite effective because of the ionic character of the system. The 1*s*-like and 2*s*-like bands can be treated as purely atomic. (The discrepancy between atomic and 1*L* values for the contribution from these bands is less than one percent in the stopping cross section at its maximum). The three energy bands of 2*p*-like character all lie in a similar energy range, hence were treated as one energy window. This grouping was tested by partitioning the same energy range into three equal windows

TABLE IV. Comparison of the phase difference in proton stopping by LiF-1L, LiF molecular, and Bragg rule (superposed Li and F atoms) targets. The units for S are 10^{-15} eV cm^2/molecule. Asterisks denote two energy levels are for two spins.

		Li atom +F atom		LiF quasimolecule; molecule along x direction	LiF monolayer
		F atom	Li atom		
KS bases		13*s*8*p*	13*s*	13*s*8*p*1*pz* for F 13*s*4*p* for Li	13*s*8*p*1*pz* for F 12*s*4*p* for Li
Q and *Xc* bases				13*s*7*d*3p_x for F 12*s*4*d*2p_x for Li	13*s*7*d* for F 11*s*4*d* for Li
distance between Li and F (a.u.)		arbitrarily large		2.80	3.50
$E_{\text{tot}}(H)$		−106.473 22		−106.713 20	−106.815 08
F-like 1*S* band	Energy range (H)	−24.198 04 −24.167 38*		−23.922 76	from −24.009 58 to −24.009 58
	I (eV)	483.498		483.682	483.651
	S at $v=2.25$ a.u.	0.160		0.160	0.160
Li-like 1*s* band	Energy range (H)		−1.875 35 −1.867 29*	−1.819 28	from −1.754 48 to −1.750 41
	I (eV)		71.424	72.493	72.580
	S at $v=2.25$ a.u.		2.745	2.745	2.778 (film)
2*S* band	Energy range (H)	−1.115 86 −1.055 27*	−0.124 63 −0.048 07*	−0.898 22	from −0.994 72 to −0.971 30
	I (eV)	62.550	3.420	62.943	62.465
	S at $v=2.25$ a.u.	3.991	8.072	4.054	4.108
2*p* band	Energy range (H)	−0.444 10 −0.385 25*		from −0.252 08 to −0.226 04	from −0.386 50 to −0.285 74
	I (eV)	54.363		48.184	50.688
	S at $v=2.25$ a.u.	8.034		11.314	10.923
I^{total} (eV)		91.148	25.935	79.308	81.134
S^{tot} at $v=2.25$ a.u.		23.002		18.273	17.936
$S_{\max}$		40.489		18.290	17.962
v at $S_{\max}$ (a.u.)		0.61		2.32	2.33

$E_{l-1} \leq \varepsilon_{j,\mathbf{k}} \leq E_l (l=1,2,3$ and $\varepsilon_{j\mathbf{k}}$ is the band energy) according to

$$E_l = E_{\min}^{2p} + l[(E_{\max}^{2p} - E_{\min}^{2p})/3], \quad l=0,1,2,3 .$$

$S(\mathbf{v})$ at one velocity (near the position of its maximum as found in the single-window calculation) was calculated with this three-window partitioning. Again the discrepancy between the two treatments was only in the second decimal place in the stopping cross section at that velocity.

As with other molecular properties, the stopping for the isolated molecule was treated via FILMS calculation for the LiF "quasimolecule" system discussed above [but with the Hedin-Lundqvist (HL) LDA for consistency].

Figure 5 shows the stopping cross sections as a function of proton velocity for the 1*L*, the molecule, and for superposed atoms. (The energy windows, mean excitation energies, and maximum stopping cross sections for the LiF-1*L*, the LiF quasimolecule, and the Li and F atoms are found in Table IV.) The predominant qualitative feature is the closeness of the stopping cross section for the LiF-1*L* and the molecule; the latter is about 3% larger at most. Though this behavior differs from that of both metallic and covalent 1*L*'s, it is unsurprising since the total energy of the molecule is close to the total energy per formula unit of the 1*L* and the valence band for the 1*L* is rather flat. These features all reflect the fact that most of the binding is intramolecular.

Dominance of stopping by molecular binding is shown quite dramatically in Fig. 5. It shows that the Bragg rule, namely, the assumption of superposition,

$$S_{AB}(v) \approx S_A(v) + S_B(v)$$

with S_A, S_B from atomic Li and F, respectively, overestimates both the 1*L* and isolated molecule stopping greatly. Since the molecular and 1*L* stopping differ little, it is clearly the molecular binding effects omitted from the Bragg rule which cause the large differences. Experimental results[60] for stopping in thin evaporated layers of boron-doped LiF agree with Andersen and Ziegler's[67] predictions within a few percent if the Bragg rule is used with ionic input. Because of the LDA problem with free negative ions discussed above, we could not perform the analogous test. The localized charge distribution of the LiF-1*L* and its overall dominance by molecular behavior are consistent though with the expectation that the Bragg rule with ionic input would give a reasonable description of these systems.

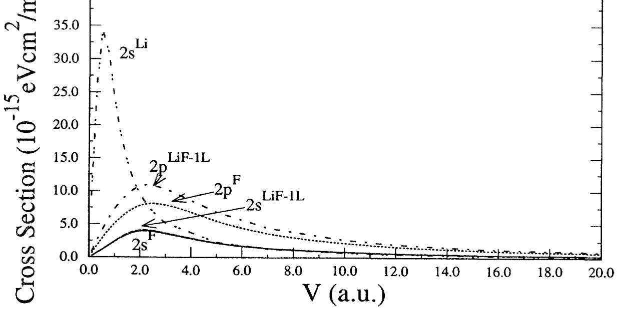

FIG. 6. Comparison of the 2*s* stopping and 2*p* stopping for the F and Li atoms and corresponding contributions for the LiF-1*L*.

Finally, the shift in 2*s* and 2*p* stopping from the isolated Li and F atoms to that of the LiF-1*L* makes evident the extent to which the 2*s* and 2*p* orbitals of LiF are dominated by F contributions. In Fig. 6 one sees that the 2*s*-like stopping for the LiF-1*L* is almost the same as that of the F atom. The 2*p*-like stopping in the 1*L* has the same behavior but is bigger than that for the F atom, a consequence of charge transfer.

VI. SUMMARY AND CONCLUSIONS

Ionic binding in the context of the planar coordination intrinsic to the LiF-1*L* results in a lattice constant contracted relative to the crystal (3.50 a.u. versus 3.86 a.u.). The large lattice contraction is traceable to a qualitative difference between the crystal and the 1*L*. In rocksalt, each ion has six nearest neighbors of opposite sign and twelve second neighbors of the same sign, while the (100) 1*L* from rocksalt has equal numbers of nearest neighbors of opposite sign and second neighbors of the same sign. In the point charge approximation, therefore, the 1*L* is attractive through two shells of neighbors while the crystal is not. Thus, this contraction may be an indication of real difficulty in epitaxial growth of LiF, since adsorbed layers inevitably will be at high stress. There is another consideration, however. Relative to the crystal there is also substantial constriction of the bonding charge distribution into the nuclear plane (0.033 e/a.u.^{3} at the density minimum along the Li-F axis versus 0.023 e/a.u.^{3} for the crystal) but the density minimum occurs at essentially the same fraction (61.1% from F) of the Li-F axis as in the crystal (61.6%). The much reduced out-of-plane extent of the charge density suggests at least the possibility of epitaxial growth of LiF at much constricted lattice constants, because of the possibility of reduced interaction with the substrate.

The 1*L* band gap is indirect (9.8 eV scaled from bare KS value) whereas the crystalline gap is direct (13.6–14.2 eV, measured). Perhaps fortuitously, Roy, Singh, and Gallon found an electron energy loss peak in both cleaved single crystals and vacuum deposited films of LiF at 10.4 eV.[68] They made a tentative identification with the surface exciton and deduced therefore a surface band gap some 3.1 eV smaller than the bulk value. The values calculated here at least are consistent with that reduction. Interestingly, the 1*L* charge transfer is estimated to be 0.87 electrons, that is, very little different from reported molecular values.

All of these features are consistent with bonding dominated by formation of the diatom constituent, a perspective which is validated from calculation of proton stopping by the electron population. Bragg rule superposition works well when molecular LiF stopping is compared with the 1*L* but not at all when atomic Li and F stopping powers are superposed. The Bragg rule therefore is useful only if the bonding in a system is understood *a priori.*

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