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Optical-absorption and photo emission edges in insulating solids*

A. Barry Kunz

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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In this paper, the author considers in general terms the theory predicting the position of optical-absorption edges and also photoemission edges in insulating solids. It is seen that these two experimental techniques may probe fundamentally different properties of solids and that by proper analysis of these results it is possible to deduce directly the effects of "excitonic" processes in soft-x-ray spectra. By constructing appropriate limits of the general theory, it becomes possible to perform a series of model calculations for several systems to illustrate the salient features. In general, a very favorable comparison with experiment is obtained. Based upon these models, one is also able to give a quantitative size to such various effects as relaxation, correlation, and electron-hole interaction strength. Finally, we are able to resolve the controversy among Brown *et al.*, Menzel *et al.*, Åberg and Dehmer, and Kunz *et al.* in favor of the excitonic model for explaining the optical absorption spectrum of LiF.

I. INTRODUCTION

The study of optical-absorption edges in insulators has consumed a considerable amount of effort in the past ten years. By this statement, the author includes soft or even hard x-ray edges in the class of optical-absorption edges. Of course, in the recent few years most of the effort has been concentrated on the soft-x-ray region of the spectrum, a region which, until the advent of convenient synchrotron radiation sources, was most difficult to study.

Most of the experimental work has concentrated upon ordinary optical-absorption experiments. Especially in the soft-x-ray region there has been an absence of any experiments using modulation spectroscopy techniques or two-quantum absorption studies, which permit one to identify to some extent the symmetry and the character of the transitions in question. Thus, for example, in the soft-x-ray region it has not been possible to unequivocably establish the presence or absence of excitonic transitions which dominate the optical-absorption spectrum of an insulator in the region of fundamental optical absorption.

Another class of interesting and useful experiments which are performed are ESCA (electron spectroscopy for chemical analysis) or the x-ray photoemission (XPE) experiments. In this type of experiment the sample absorbs an energetic photon and the kinetic-energy distribution of the emitted electrons is analyzed. In such an experiment when subject to proper analysis, the energy distribution of the initial states may be deduced, and also sometimes that of the conduction states, provided they overlie the ionization continuum. The essential difference between an ESCA or an XPE measurement involves the type of photon source and is of no concern for the present time.

This paper is in part being written to illustrate some limitations on interpretation of the absorption- or the emission-type experiments and to illustrate how the two techniques may be used in conjunction to discuss questions of the excitonic nature, or not, of the absorption edges.

Consider the following example. The crystal in question is LiF, and we may wish to know experimentally the energy separation between, say, the Li K shell (1s shell) and the fluorine $L_{II,III}$ shell (2p shell or the valence band). One could imagine measuring this in two or three ways. In the first of them, which has been performed in part by Stephan[1] and by Sonntag,[2] one measures the onset of optical absorption from the F $L_{II,III}$ shell and also from the Li K shell. One might then interpret the difference in these energies as being the energy difference between the K shell and the $L_{II,III}$ shell. In the present case, the K-shell absorption begins at about 54 eV while the $L_{II,III}$-shell absorption begins at about 12 eV, yielding a difference of 42 eV for the splitting between the K shell and the $L_{II,III}$ shell. The alternate is to study the XPE spectra of these shells as has recently been done by Gudat *et al.*[3] In this case, one finds that the splitting of the K shell and the $L_{II,III}$ shell is 50 eV. Clearly there is some difference here. In addition, one might also do a direct measurement by partly depopulating the K shell and then measuring the energy of photons emitted as electrons from the $L_{II,III}$ shell fall into the K shell. This measurement would in principle yield a still different result. The difference between these results is not, in the author's opinion, due to any lack of experimental precision, but is a direct measure of the strength of electron-hole or excitonic interaction in these crystals.

Here it is known from valence-band excitations that the strength of the excitonic effect (binding energy) in this region of the spectrum is about 0.5–2 eV. This shall be shown to mean, in effect, that in the soft-x-ray region of the spectrum, the strength of such exciton effects is about 10 eV, or hence about the first 10 eV of the soft-x-ray spectrum must be due to either localized atomiclike excitations or excitons.

The theoretical situation has been much more fragmentary. It was first observed by Brown *et al.* that the shapes of the soft-x-ray absorption spectra bore great resemblance in many but not all cases to the density of states of the conduction band.[4] This idea has been extended by the present author for the alkali halides,[5] by Rössler for the rare-gas solids,[6] and by the author and Mickish for these cases.[7] Most recently, Menzel *et al.* have advanced the idea of band structure for LiF being entirely responsible for the optical properties (in both fundamental and Li *K*-shell region).[8] However, as we see from the preceding analysis of data for LiF, the theory of Menzel *et al.* becomes impossible since if band theory were correct, the ESCA and absorption data would agree. Analysis of a type like that used in this article to sort exciton from band effects using experimental data rather than theory was done for RbCl by Scheifley and Brown.[4] This work of Scheifley was greatly hindered by a lack of quality band theory for RbCl.

Alternate studies of soft-x-ray spectra in insulators, and particularly those intent upon predicting absorption peak positions have been either of a deep-impurity type[9–13] or of the more usual excitonic type.[13,14] In such calculations or theories, the shape of absorption spectra is usually secondary to the question of line positions. In addition, there have been some exciton theories based upon critical-point type analysis advanced by Onodera and Toyozawa[15] in which splittings of exciton lines formed from band states at critical points are studied for both electrostatic and spin-orbit interactions. It shall be seen that for such crystals as considered in the present case the strength of the electron-hole interaction and the localization of the low-lying exciton-excited states are such that critical-point analysis becomes pointless in many instances.

Finally, in this rundown of pertinent preliminary results, the author refers to the results of the calculations using the operator $\hat{O}\hat{A}\hat{O}$ of Collins and Kunz.[16] In this, the strength of Coulomb hole interaction was studied for atomic excitations. It was found, in general, that these effects were substantial. It was also found by a comparison of these results to experiment that simple atomic relaxation or polarization effects were exceptionally large and, in fact, for many core excitations, there relaxations far exceeded the strength of the electron-hole interaction for such states. It was also seen then that a simple dielectric theory added to the electron-hole interaction, in order to describe the polarization relaxation, would involve a dielectric constant less than unity if such a description were to succeed. No one seems anxious to use such a dielectric constant. This indicates that simple, effective-mass type theories for core-exciton formation is pointless in most, or at least many, cases.

In the present paper, in Sec. II, we consider general theoretical considerations. The author examines this both from the standpoint of ordinary energy-band theory and also from the viewpoint of a Heitler-London theory. In Sec. III, the author takes the general considerations of Sec. II and reduces them to solvable models which are used in the present study. In Sec. IV, the author provides a series of atomic-system calculations which illustrate the theoretical features of the present ideas. In Sec. V, a number of solid-state calculations are performed in which a quantitative value is placed on a variety of pretinent effects as well as experimental quantities. In Sec. VI, the present theories are extensively compared to experiment. Finally, in Sec. VII, the author draws his conclusions. Throughout this paper, the author neglects lattice-relaxation or lattice-dynamical effects. It is not, however, to be inferred from this neglect that the author considers such effects unimportant, but rather they serve simply to modify the dominant electronic effects discussed in this paper by amounts which are comparable in size to the errors introduced by the approximation to the larger electronic terms.

II. GENERAL THEORETICAL CONSIDERATIONS

In this section the author constructs a brief theoretical review from rather general points of view. On the whole, such viewpoints are not to be regarded as new but are, nonetheless, not so completely assimilated by the scientist as to make such a review superfluous. In the later stages of this work it shall be advantageous to adopt different viewpoints for purposes of economy in computing different contributions. Therefore, it is of some use here to study the question of band theory and exciton formation from both the molecular-orbital (Bloch orbital) and from the Heitler-London (or general valence bond) point of view. There are any number of places where the information conveyed here is available in greater detail. Perhaps the most accessible is that of Knox.[17]

In our calculations we view the solid as being described in the first approximation by a single Slater determinant of one-electron orbitals. If these orbitals are suitably chosen via the variational theorem, subject to constraints of orthonormality, one may obtain the one-electron orbitals as being given by the canonical unrestricted Hartree-Fock formalism. In this case, the one-electron eigenstates are symmetry adapted (i.e., they have the periodicity of the lattice), and generally each one spans all the infinite periodic lattice. It turns out that these orbitals are a convenient set for describing properties such as conductivity but much less convenient for describing localized phenomena. If the orbitals are chosen such that

$$F(\rho)\phi_i(x)=\epsilon_i\phi_i(x)\ , \tag{1}$$

where $F(\rho)$ is the Fock operator for the system, then one has

$$\int\phi_i^*(\vec{x})\phi_j(\vec{x})\,d\tau=\delta_{ij}\ . \tag{2}$$

Now one allows $\vec{x}$ to stand for both spatial dependence $\vec{r}$ and spin dependence $\vec{s}$ of the orbitals, and $\int d\tau$ includes summation over spin coordinates. One recognizes that some solutions to Eq. (1) define orbitals which have electrons in them (occupied orbitals) in the ground state as well as unoccupied states (virtual orbitals). I assume here N electrons in the system and use the notations $\cdots i,j\cdots \leqslant N > \cdots a,b\cdots$ with the i,j labeling occupied orbitals and the a,b being virtual orbitals.

In terms of this notation the first-order density matrix is defined

$$\rho(\vec{x},\vec{x}')=\sum_{i=1}^{N}\phi_i(\vec{x})\phi_i^\dagger(\vec{x}')\ . \tag{3}$$

From this one has some immediate physical consequences which are summed up in Koopmans's theorem. These consequences are that if all the orbitals ϕ_k and ϕ_c are chosen from a self-consistent solution of Eq. (1) for the ground state, then in this frozen-orbital limit the eigenvalues ϵ_k represent the energy needed to remove the electron in orbital k from the system. That is, one goes from an N to an $N-1$ body system. The eigenvalue ϵ_a represents the energy needed to add an electron to the system, putting it in an orbital a. Thus one goes from an N- to an $(N+1)$-body system.

In much usual solid-state physics, one also identifies the energy difference $\epsilon_a-\epsilon_i$ as being the amount of energy needed to excite an electron from state i to state a. This identification is only justified if the orbitals span all of an infinite periodic lattice whereby the effect of changing the number of particles on the potential is totally negligible. The above descriptions constitute what is generally regarded as Koopmans's theorem.[18] The consequence of this is to say that the usual Hartree-Fock virtual orbitals do not see any electron-hole interaction. It has been recently shown that the absence of electron-hole interaction in a simple Hartree-Fock system, such as given by Eq. (1), is a consequence of an arbitrary choice for the virtual manifold rather than as a consequence of Hartree-Fock theory, and there is a proper choice of F which permits one to obtain virtual states which see electron-hole interactions, possess a real Koopmans's theorem for excitation even for localized states, and satisfy a variational principle.[19]

One recognizes that the Hartree-Fock system so far described possesses several defects even if electron-hole interaction is properly included. These defects are, of course, when one uses Koopmans's theorem, one neglects the relaxation of the other orbitals and hence the associated energy changes of the rest of the system. This correction is termed a relaxation correction and stems solely from not performing self-consistent calculations on both ground and excited state or alternately on both ground and ionized state. The second defect is that all dyanmic correlations between electrons are neglected. The correlation and relaxation corrections are together taken to be the self-energy correction. It is normal for extended systems then to solve beyond Hartree-Fock by solving Dyson's equation, to which Hartree-Fock is the first approximation.[20] Thus if e_i is the actual energy of the electron in state i, one has

$$e_i=\epsilon_i+\Sigma_i^*\ , \tag{4}$$

Σ_i^* being the self-energy.

III. DEVELOPMENT OF SOLVABLE MODELS

In this section, the author will derive a series of reasonably simple, solvable models for the phenomena of optical absorption and for photoemission experiments. In this case, development is made starting with both the band-theoretical model (molecular orbitals) and the Heitler-London formalism (valence-bond model). The author will, in the case of correlation, rely heavily on previous efforts.[21]

A. Correlation corrections

One begins with the molecular orbital model and includes correlation as required. Traditionally this is done in two ways. The first way which is termed screended-exchange plus Coulomb-hole was given useful formulation by Hedin[22] and was used first on a calculation for Si.[23] This model was later extended as an adjunct to a Hartree-Fock formalism by Lipari and the author.[5,24–26]

The second model used is that of the electronic polaron (EPM), which was introduced for the case of conduction electrons by Toyozawa,[27] and given a fundamental derivation and extended to the case of holes by the author.[28] In this model, the correlation contribution to Σ^*, called $\Sigma_{nc}^*(\vec{k})$, is found to be for conduction electrons

$$\Sigma_{ac}^*(\vec{k})=\sum_{\vec{q},b}\frac{|V_{\vec{q}}^{ab}|^2}{\epsilon_a(\vec{k})-\hbar W_{\mathrm{ex}}-\epsilon_b(\vec{k}-\vec{q})}\ , \tag{5}$$

and for holes

$$\Sigma^*_{nc}(\vec{\mathrm{k}}) = \sum_{\vec{\mathrm{q}},m} \frac{|V^{nm}_{\vec{\mathrm{q}}}|^2}{\epsilon_n(\mathrm{k}) + \hbar W_{\mathrm{ex}} - \epsilon_m(\mathrm{k}-\mathrm{q})} , \tag{6}$$

where

$$V^{nm}_{\vec{\mathrm{q}}} = e\left(\frac{2\pi\hbar W_{\mathrm{ex}}(1-1/\epsilon_\infty)}{V}\right)^{1/2} \times \frac{i}{|\vec{\mathrm{q}}|}\int \phi^*_n(\vec{\mathrm{r}})\,\phi_m(\vec{\mathrm{r}})\,e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}}\,d\vec{\mathrm{r}} . \tag{7}$$

In this case the summation on $\vec{\mathrm{q}}$ is over the first Brillouin zone. For electrons the b summation extends all conduction levels and for holes the M summation is over the occupied space. V is the crystal volume, e the electron charge, ϵ_∞ the optical dielectric constant, ϕ_i is the Wannier function for the ith band, and $\hbar W_{\mathrm{ex}}$ is the quantum of the polarization field (in this instance, the longitudinal exciton field) and is assumed dispersionless. This model is valid in so far as the width of the band being correlated is less than $\hbar W_{\mathrm{ex}}$. This method of correlation may be generalized and even extended to the case of metallic systems.[29]

It is clear that it is also possible to develop a definition of the energy-band model from a valence-bond or Heitler-London point of view. To the best knowledge of the author, no such band calculations have been carried out at the present. It is noted that the structure of the energy-band Hamiltonian as a function of wave vector here is similar to that for the molecular-orbital case. Furthermore, in the unrelaxed orbital limit one would expect, for insulators, that the energy bands would be quantitatively, as well as qualitatively, similar to the molecular-orbital case. Correlation corrections based upon the Heitler-London model are not fully developed. There is, however, an available limiting theory of such a model due to Fowler.[26] In this model (a semiclassical one), the electron charge is situated at either a cation or anion (or atomic) site, and the atom or ion at this site is neglected. The remainder of the crystal is then treated as if it were consisting of a collection of nonoverlapping polarizable ions (or atoms). The polarization of this assemblage is computed, as is the energy associated with this polarization. This energy is then identified with Σ^*_c. Clearly this model neglects $\vec{\mathrm{k}}$ dependence. It does, however, distinguish between events on nonequivalent lattice sites. Most importantly, this model clearly and unequivocably neglects the effects of relaxation on the ion or atom at the origin and, most importantly, this model is seen to be equivalent to the electronic polaron model if one takes a static limit of the electronic polaron (i.e., that limit in which the bands are dispersionless).

It is also necessary to make a brief comment about the agreement found among the various correlation models. At this point, there are a number of calculations of Σ^*_{ic} using all three models for the same crystal. First, these models are in excellent qualitative agreement. Second, for the number of crystals for which all three types of results are available and computed in a seemingly reliable manner, one finds that roughly Σ^*_{ic} serves to lower the band gaps by about 4.0 ± 1.0 eV and that the agreement on this quantity among the models is of the order of 10%. For most practical purposes, this level of agreement is adequate.

It is necessary at this point to say a word about the presumed local states which occur as virtual levels in the Heitler-London scheme. The virtual orbitals, if the ϵ matrix for the virtual states is to be diagonal, are just the ordinary virtual Bloch functions. This is undesirable for a localized description and unnecessary. The virtual levels are arbitrary. Let one define

$$\hat{O} = 1 - \rho , \tag{8}$$

$$A^{1-F} = \hat{O}\hat{A}\hat{O} , \tag{9}$$

then let one solve,

$$(F + \rho\hat{U}\rho + \hat{O}\hat{A}\hat{O})\phi_{Ai} = \epsilon_{Ai}\phi_{Ai} . \tag{10}$$

Here both $\hat{U}$ and $\hat{A}$ are arbitrary Hermitian operators. However, if $\hat{A}$ is chosen to be attractive and to interrupt the periodicity of the lattice, one can obtain localized virtual states from Eq. (10). Some particularly useful choices for $\hat{A}$ based on physical consideration are given by Kunz and Collins.[16,19] One may consider Eq. (10) to be the generalized Hartree-Fock equation.

B. Relaxation models

The basic problem of relaxation can be handled, in principle, from the viewpoint of the molecular-orbital approach. In the case of atoms or molecules, it is standard to include relaxation corrections totally by the simple expedient of solving for the ground and the excited or ionized states of the system in fully self-consistent calculations. In such calculations, the differences in total energies include not only Koopmans's terms but also complete relaxation information. In addition, for the case of excitation, such a calculation also includes the electron-hole interaction in a manner which is correct, save for the inclusion of correlation corrections. In the cases of deep-core states especially, correlation corrections have been seen to be minor compared to other effects and the answer based upon the total energy difference of self-consistent calculations has been capable of great precision.[30] In the case of the infinite solid with its infinite total energy, such a simple and direct calculation has thus far been impractical. Of course, such difficulties as infinities may be avoided in the direct approach with molecular orbitals by using a perturbation expansion in terms of unrelaxed orbitals and thereby directly cancel the infinities prior to calculation. To date, no one has actually performed such a calculation for any real solid.

A more simple and direct method for constructing the effects of relaxation is possible if one considers the Heitler-London model. In what follows, the author relaxes the restrictions that the orbitals used in the excited state or for the ionized states be obtained from solving self-consistently Eq. (10) for the orbitals. Instead, the author assumes that Eq. (10) is solved self-consistently for the ground state, as is true for a number of solids now. One proceeds by permitting the orbitals in the wave functions given by Eq. (10) to be chosen variationally by minimizing the energy of the Hamiltonian with respect to these wave functions.

To do this, one proceeds as follows, which is very similar to the derivation of the multiconfigurational self-consistent-field equations by Gilbert,[31] except that in the present case the coefficients of the single Slater determinant (called patterns by Gilbert) are constrained by symmetry considerations within a multiplicative factor of modulus unity. The total energy is represented as

$$E=\langle\psi|\mathcal{H}|\psi\rangle=\langle f\rho\rangle+\langle\langle(g\gamma)\rangle\rangle\ , \tag{11}$$

where, in keeping with the usual usage in this type of theory, one has

$$\rho=M\langle\psi\psi^{\dagger}\rangle_{M-1}\ , \tag{12}$$

$$\gamma=\tfrac{1}{2}M\langle\psi\psi^{\dagger}\rangle_{M-2}\ . \tag{13}$$

There are M electrons, and ρ and γ are the reduced first- and second-order density operators. In proceeding, we could follow Gilbert in not constraining the orbitals to be orthogonal, but this complexity is not needed for the present case. If orthogonality is desired, the correct variational equations are simply

$$\delta\Bigl(E-\sum_{Ai,Bj=1}^{N}\langle Ai|Bj\rangle\lambda_{AiBj}\Bigr)\Big/\delta\phi^{\dagger}_{Ai}=0 \tag{14}$$

or

$$\delta\Bigl(E-\sum_{AiBj=1}^{N}\langle Ai|Bj\rangle\lambda_{AiBj}\Bigr)\Big/\delta\phi_{Ai}=0\ . \tag{15}$$

The evaluation of these variations yields the equations for the orbitals ϕ_{Ai} which become

$$F\phi_{Ai}-\sum_{Bj=1}^{M}\phi_{Bj}\lambda_{BjAi}=0 \tag{16}$$

and

$$F\phi^{*}_{Ai}-\sum_{Bj=1}^{M}\lambda_{BjAi}\phi^{*}_{Bj}=0\ . \tag{17}$$

Here the orbital operator F is found to be

$$F=f\rho+2\langle g\gamma)\ , \tag{18}$$

with

$$f\rho=\sum_{i}\int\rho(\vec{x},\vec{x}'')f_{i}(\vec{x}'',\vec{x}')\,d\vec{x}'' \tag{19}$$

and

$$\langle g\gamma\rangle=\sum_{ij}\int\!\!\int\!\!\int g_{ij}(\vec{x}_1\vec{x}\vec{x}_1'\vec{x}_2')\gamma \times(\vec{x}_1'\vec{x}_2',\vec{x}_1'\vec{x})\,d\vec{x}\,d\vec{x}_2'\,d\vec{x}_1'\ . \tag{20}$$

Finally, the author specifies that here operators are treated as local kernels, that is, for example,

$$f_{i}(\vec{x}\vec{x}')=f_{i}\delta(\vec{x}-\vec{x}')$$

and

$$g_{ij}(\vec{x},\vec{x}',\vec{x}_1,\vec{x}_1')=\delta(\vec{x}-\vec{x}_1)\delta(\vec{x}'-\vec{x}_1')g_{ij} \tag{21}$$

Equations of this nature of complexity are routinely solved in calculations for simple atoms and molecules. To date, implementation of a scheme such as outlined above has not been feasible for the general solid-state case.

What is very beneficial from the standpoint of our present considerations are the specific approximation scheme which one might devise from these considerations. It is for this reason we explicitly include the preceding discussion on Gilbert's work. Therefore, the models being employed are at least correct in some realistic limit, which, in part, justifies the inclusion of this material. This limit is one in which one assumes that the atoms or ions comprising the system overlap slightly or not at all. (Such a condition is often met in the alkali halides or solid rare gases, in which the ground-state local orbitals overlap by about 0.05 or less.) In such a nonoverlapping limit, the energy expectation value of the wavefunction (10) is about the same as for the symmetry adapted wave function. Therefore, one need not prefer at this level one wave function from the other in calculating energy differences.[32]

In this limit, consider first the case of optical excitation. Here one has the atom at site A being excited and the other atoms remain in their ground state. The ground state of the other atoms need not be the same as when the system as a whole were in the ground state. However, when one excites the atom at site A, this atom doesn't alter its state of charge, since we consider here formation of excitons rather than excitations which ionize the atom in question. If the atom is ionized, relaxation effects due to the surroundings will increase the values of the relaxation energies given in this paper.

Therefore, in the small overlap region, one may anticipate that the polarization of the surrounding atom is weak compared to that of the atom at site

A. Therefore, if all atoms other than that at site A are fixed in their system ground-state configuration, that one at site A must be solved for in the ground-state and the excited-state configuration self-consistently. The total energy difference than represents the excitation energy, and, by construction, contains the following contributions: that due to Koopmans's theorem, Hartree-Fock relaxation, and electron-hole, but no correlation, since this limit is clearly a single determinant. One may subtract the Hartree-Fock contribution and obtain the magnitude of the relaxation plus electron-hole correction. It is further possible to separate out the electron-hole interaction from relaxation. There are two ways to do this. The first is to solve for the excited state at $\hat{A}$ in the canonical Hartree-Fock limit and then, in the $\hat{O}\hat{A}\hat{O}$ limit, choose $\hat{A}$ to properly represent the hole formed.[16,19] This is a simple procedure to implement and has been done here extensively. From this evaluation of electron-hole interaction, one then subtracts from the effects of relaxation plus electron-hole to obtain the effects of relaxation alone. The second procedure is to use the ionization processes from (10) and, in the vanishing overlap limit, calculate self-consistently the energy to ionize the atom at A self-consistently in the field of the fixed other atoms.[31] From a comparison of the Hartree-Fock eigenvalue to the total energy, one has Σ^*_{Ri} directly. That is, one has

$$-\Sigma^*_{Ri}=E^{(A)}_{I(i)}-E^{(A)}_{g}+\epsilon_{Ai} \; . \tag{22}$$

This has been tested for the rare-gas systems He, Ne, Ar. It is concluded directly for the rare-gas systems that the relaxation phenomena is strictly a local atomic effect. Owing to their cost and complexity, similar calculations were not made for the alkali halides. However, one may infer a similar result from available information. Although the alkali halides overlap more strongly than the solid rare gases ($S_{nn} \lesssim 0.05$), the overlap is still quite small compared to unity. It is also well known that the cohesive energy of the alkali halides is essentially accounted for by the Madelung energy term with the detailed electron charge effects being quite insignificant[18] by comparison. Since the Madelung contribution is similar in the relaxed and unrelaxed state, and since the relaxed state is less diffuse than the unrelaxed state so that the detailed electronic structure is even less important, one argues that here too the greatest part of the relaxation energy is due to the central-cell atom (or ion) relaxation. It is true that in the ionic-crystal case the wavefunctions of the atoms around the central-cell atoms are also distorted by having dipoles induced when the state of ionization of central-cell atom changes. However, such effects are in part at least included in either a Mott-Littleton[26] or electron-polaron[27,28] model. Finally, it is also worth noting that even though the relaxation model is derived from a Heitler-London model and the correlation model from a Bloch picture that both effects as given here are distinct and contributions are not being counted twice.[26,29]

C. Electron-hole interaction

The highly approximate version of the self-consistent Heitler-London model as described in Sec. III B provides one with electron-hole interaction strengths. In fact, in the limit described which is appropriate for either an "impurity" state, or a description akin to such a state, or for the more normal symmetry adapted state, one finds the amount by which the electron-hole paired state (called hereafter an exciton whether it be an "impurity state" or a true-crystal stationary state) lies below the continuum or bandlike state. This energy difference can be expressed in terms of the $\hat{O}\hat{A}\hat{O}$ formalism as follows. Let i refer to the hole and a to the electron. Let ϵ^i_a be the $\hat{O}\hat{A}\hat{O}$ energy of electron a in the presence of hole i, and let ϵ_a be the canonical Hartree-Fock energy of orbital a. The electron-hole interaction strength is then found to be

$$K_{ia}=\epsilon^i_a-\epsilon_a \; . \tag{23}$$

In the simplest limit one would predict that the greatest amount by which the exciton line would lie below the band state is just K_{ia}. This limit clearly neglects any dispersion in the energy levels. One might, in principle, solve for the exciton state in order to correct this deficiency. Such a calculation is not currently practical, although very desirable. There are other limits which permit one to take into account the band shape.

The most simple model is the effective-mass model. In this limit, the exciton's electron is assumed to be in a very diffuse orbit so that the effective electron-hole interaction looks like that of a point charge. This is a hydrogenic model. Here one finds that F_B, the binding energy below a band extremum, is

$$F_B=(me^4/2\epsilon^2)1/h^2n^2 \; . \tag{24}$$

In Eq. (24), m is the electron-hole reduced mass, ϵ is an appropriate dielectric constant (> 1), and n is the exciton principal quantum number. In the ionic system or the solid rare gases, the radius of the principal exciton ($n=1$) is too small for the assumption leading to (29) to be valid, and the author never uses the effective-mass theory for computing $n=1$ exciton states in this paper. However, the higher states are often much more diffuse and Eq. (24) becomes tenable. One result is to use Eq. (24) to assign a limit to the position of $n=2$ levels (s or p character) as being simply 25% of the binding energy for the $n=1$ level in the effective-mass limit. Thus, in the calculations, one may assign the lower limit (the state would be raised in energy by dielectric screening far more than it is lowered by an effective mass for the electron less than an electron mass) to the $n=2$ line as being $0.25\ K_{ij}$ as given in Eq. (23).

In these crystals, the effective-mass idea is quite simple to apply to the case of core-state excitations. The effective mass of the core holes is infinite (hence isotropic). The conduction-band minima are Γ_1 states and hence also perfectly isotropic. The author notes that the effective masses actually calculated in several different directions in $\vec{k}$ space for the energy bands used here were found to be isotropic as the theory requires. In this article the effective-mass approximation is only applied to formation of $n=2$, $l=1$ excitons (p excitons) obtained by exciting core electrons. It is believed this is reasonable here in that the p excitons are far more diffuse in $\vec{r}$ space than are the $n=1$, $l=0$ (s excitons) which we compute in the one-band–one-site model discussed below, and hence satisfy more nearly the criterion for validity of effective-mass theory. It is also noted that owing to the essential nature of the one-band–one-site model, only a single bound state is found for any of the cases considered here, so that effective-mass ideas are the only simple way to construct p excitons.

There is a second limit which is appropriate for positioning the $n=1$ exciton line in many crystals for which Eq. (24) is inappropriate and which is always employed here. This is the tight-bound limit or Slater-Koster one-band–one-site model.[33] This is a deep impurity model limit in which the crystal band structure is correctly taken into account. In this model, one assumes that the excited electron is attracted to the hole by a Coulomb interaction, that the hole is local to an ion or atom site, and that the wave function for the electron may be expanded in terms of the one-electron band orbitals. It is assumed the interaction is short range,[34] and only orbitals of a single band are used in the actual expansion. One further assumes from the band function that one constructs the appropriate Wannier functions on a given site. It is assumed then that the matrix elements of the electron-hole interaction in the Wannier representation are given by

$$\langle \vec{R}_\mu , n | V | \vec{R}_\nu , m \rangle = V_0 \delta \mu\nu \delta_{nc} \delta_{mc} \delta_{\mu 0} , \tag{25}$$

where V_0 is the effective interaction and may be given by K_{ia} in an $\hat{O}\hat{A}\hat{O}$ calculation. Here $|R_\mu , m\rangle$ is the mth Wannier function at site $\vec{R}_\nu$ and site $\vec{R}_0$ is the site of the "impurity." The quantum number c stands for the conduction band for which the sum is over. In this representation the probability that the electron is in the cell with the hole is given by[35]

$$|\psi_E(0)|^2 = |1 - V_0 \Lambda(E)|^{-2} , \tag{26}$$

$$\Lambda(E) \equiv \lim_{\delta \to 0^+} \int_{-\infty}^{\infty} \frac{dt\, N(t)}{(E - t + i\delta)} . \tag{27}$$

In (27), $N(t)$ is the state density for the bands defined by $|\vec{R}_\nu , c\rangle$.

One sees at once that in the nonoverlapping limit the quantity V_0 in (25) and (26) is identified with K_{ia} given in (23) for our model. Thus one defines the needed parameters. The author assumes that continuing to identify K_{ia} with V_0 in the small overlap limit introduces negligible error in the cases on hand.

IV. ATOMIC ILLUSTRATION

The theory outlined in Secs. II and III makes a number of definite predictions. For example, removing an electron from state 1 requires energy in the amount $(-e_1)$

$$e_1 = \epsilon_1 + \Sigma_1^* . \tag{28}$$

The energy needed to excite an electron from a state 1 to a state 3 becomes

$$E_{13} = \epsilon_3 + \Sigma_3^* - \epsilon_1 - \Sigma_1^* - K_{13} . \tag{29}$$

The expression (28) is pertinent for studies of ESCA or photoemission spectroscopy, whereas it is (29) which is pertinent for optical absorption or

TABLE I. Summary of calculations for the atomic Li and Be systems. Results of several calculations are given here for total energies in several ground and excited states. All calculations are by means of the unrestricted Hartree-Fock formalism. Energy differences between the $1s$ and $2s$ level as deduced by optical absorption, photoemission, and for Li direct transition from $1s$ to $2s$ level are also given. Results are in rydbergs.

	State		Energy
Li	$1s^2 2s$	^2S	14.8609
Li	$1s^2$	^1S	14.4710
Li	$1s2s$	^3S	10.1008
Li	$1s2s$	^1S	10.0417
Li	$1s^2 3s$	^2S	14.7499
Li	$1s2s3s$	^2S	10.2129
Li	$1s2s^2$	^2S	10.6140
Be	$1s^2 2s^2$	^1S	29.1356
Be	$1s^2 2s$	^2S	28.5454
Be	$1s2s^2$	^2S	20.0570
Be	$1s^2 2s3s$	^1S	28.6988
Be	$1s2s^2 3s$	^1S	20.2651
Li	$\Delta E(1s2s)$ for photoemission		4.3702, 4.4293
Li	$\Delta E(1s2s)$ from optical absorption to $3s$ level		4.5370
Li	$\Delta E(1s2s)$ for direct absorption		4.2469
Be	$\Delta E(1s2s)$ for photoemission		8.4884
Be	$\Delta E(1s2s)$ for optical absorption		8.4437

emission. It is thus possible to see one other effect of interest. Suppose one is interested in the separation of two occupied levels, say (1) and (2). This could be determined indirectly from either ESCA or optical absorption. For ΔE_{12} by ESCA one has

$$\Delta E_{12} = \epsilon_2 + \Sigma_2^* - \epsilon_1 - \Sigma_1^* \ , \qquad (30)$$

whereas by optical absorption one has

$$\Delta E_{12} = \epsilon_2 + \Sigma_2^* - \epsilon_1 - \Sigma_1^* + K_{13} - K_{23} \ . \qquad (31)$$

Furthermore, if direct optical absorption is possible from the level 1 to 2 (e.g., for a Li atom $1s$ to $2s$ is possible), one has

$$\Delta E_{12} = \epsilon_2 + \Sigma_2^* - \epsilon_1 - \Sigma_1^* + K_{12} . \qquad (32)$$

In general, there is no reason to expect these three expressions for ΔE_{12} to agree. It is noted however, that if one uses Eq. (31) to determine the Rydberg series limit, then the values for ΔE_{12} from Eq. (31) will agree with those from Eq. (30) since the K's vanish in this limit. However, they will not agree with the results from Eq. (32), in general. The author suggests that a criterion such as this could serve as an experimental distinction between exciton levels and band levels. Such a criterion is often needed in the soft-x-ray range since the excitons (or states analogous to deep impurities which we don't differentiate) are resonant states, and hence such traditional tests as photo conductivity are not useful for making distinctions.

To test these ideas in a simple framework, a few simple atomic calculations were performed. These were done for the Li atom and the Be atom. In this case, the energies of the various states of single ionization were computed, as were the energies of the lowest excited state for each occupied level, and, for Li, the energy of the transition $1s^2 2s \to 1s 2s^2$. All calculations were performed in the unrestricted Hartree-Fock limit. A common basis set for all Li cases is used and likewise for Be. In all cases a basis of ten Gaussian orbitals is used. In Li several possible spin states are sometimes given. From these self-consistent total energies the author calculates ΔE_{1s2s} for these systems as pertinent for the types of experiment outlines above. These results are summarized in Table I. The disagreement among the various models to define ΔE_{1s2s} is of order 1–4 eV, an amount which is significant. In Sec. V, this study is extended to solid systems and the author shows how in solid state cases this disagreement may be greatly enhanced.

V. SOLID-STATE SYSTEMS

In the event of excitation of solid-state systems the author predicts that there should be two distinct types of behavior. The first of these is analogous to the atomic system discussed in Sec. IV. In this type of system one expects the separation of core levels to be experiment dependent, but by about 1.0 eV or so. Such systems would be typified by the solid rare gases, and the author expects will include most, if not all, nonionic systems, that is, systems in which exciton formation has the electron and hole on the same site. The second type of system would be the ionic crystals which are typified by the alkali halides. In such systems, one will have markedly different behavior depending upon whether it is the anion or cation which is excited.

Consider the limit of vanishing overlap. If the ion being excited is an anion (here a negative ion), it will generally not possess any bound states other than the ground state. Therefore the electron migrates from the anion and may be trapped on the surrounding cations. If this occurs because of the charged lattice, there still exists a net Coulomb attraction between the excited electron and the now neutral anion. In this case, the Coulomb hole term is roughly but reasonably well described by the expression

$$K_{ij} = -e^2/|\vec{R}_a - \vec{R}_c|\epsilon \ . \qquad (33)$$

In Eq. (33), $\vec{R}_a - \vec{R}_c$ is the average separation of anion and cation, and ϵ is put to include the effect of screening which reduces the size of the attraction. In the present model calculations, where pertinent, the author uses the optical dielectric constant which serves to maximize K_{ij}. In general, there is additional screening owing to ionic motion which would enhance ϵ above the optical limit. Thus, in general, the value given by the author for excitation of anions will be an upper bound on the exciton binding (lower bound on the exciton position).[36]

In exciting the cation, things are much different. The cation itself has a Coulomb attraction for the excited electron, and hence an infinite number of bound states on the same ion as the hole. In this case, the value of K_{ij} is given as described in Sec. III C. Because of these physically different mechanisms for ionic crystals, the discrepancies in energy between core levels as determined by differing processes can vary substantially, and are found to differ by as much as 10 eV or so. The author would anticipate that such effects would be present in polar molecules to a degree similar to the ionic crystals. In the remainder of this section, the author describes the results of specific calculations for the solid-state systems, Ne, Ar, LiF, NaF, KF, LiCl, NaCl, and KCl. In these calculations the author will ignore the small differences between levels as typified by the atomic calculations in Sec. IV. The reader should be aware of their presence. In the methods used here such splittings for these

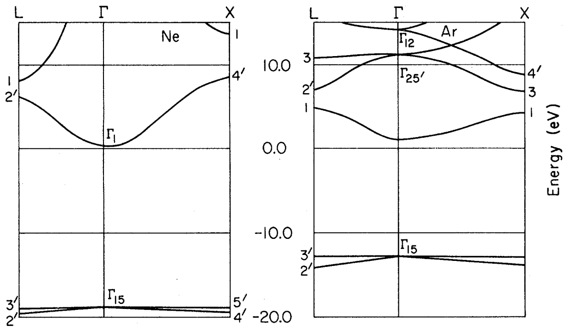

FIG. 1. Correlated energy bands for solids Ne and Ar are given from Ref. 5.

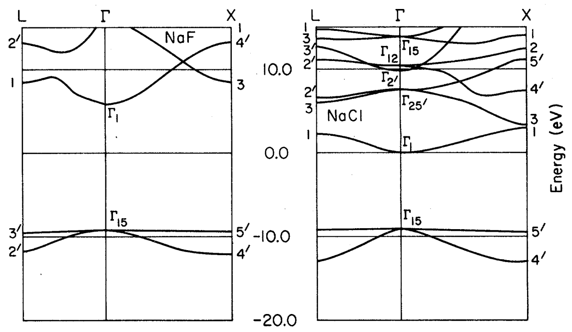

FIG. 3. Correlated energy bands for NaF and NaCl are given from Ref. 5.

solids were of the order of 0.25 eV. He concentrates instead on the larger effect of charge transfer versus non-charge transfer and in calculating the absolute position of true band absorption edges, lower bounds for exciton absorption for the band edges, in some cases actual positions of exciton lines using the theory of Sec. III C, and the positions for ESCA-type edges. The actual models used here are the following. The bands are computed first in the restricted Hartree-Fock limit. For the substances here these calculations are available, and hence no new calculations of this type are performed. The correlation part of Σ^* is evaluated by the EPM except for NaCl and KCl, for which the available Coulomb hole plus screened exchange results are used, and for occasional core levels where Fowler's results are used.[26] The relaxation part of Σ^* is evaluated using the Heitler-London approximation given in Sec. III B. The K_{ij}'s come from the $\hat{O}\hat{A}\hat{O}$ of Sec. III C, except for the charge transfer states, for which Eq. (47) is used. In using the Lipari and/or Kunz[5] results for LiCl, NaCl, and KCl, the valence bands are recomputed in position to correct for poor convergence of the plane-wave basis in the original calculation. It is noted in passing, such corrections aren't needed for LiBr and NaBr of Lipari and Kunz,[5] as these are better converged.

Finally, the author will discuss the practical aspects of applying the $\hat{O}\hat{A}\hat{O}$ model to compute the electron-hole interaction strength. In doing this, the author briefly summarizes a series of theorems proven in Ref. 19 by Kunz and Collins. According to Ref. 19, the proper choice of the operator $\hat{O}\hat{A}\hat{O}$, is given by

$$\hat{O}\hat{A}\hat{O}=\hat{O}[(-1)\langle n|g_{12}(1-P_{12})|n\rangle]\hat{O}\ , \qquad (34)$$

where one defines P_{12} by

$$\langle a|\hat{O}\langle n|g_{12}P_{12}|n\rangle\hat{O}|a\rangle\equiv\langle an|g_{12}|na\rangle\ . \qquad (35)$$

In Eq. (36), g_{12} is the two-body operator $(e^2/|\vec{r}_{12}|)$ and $|n\rangle$ is the wave function for the hole vacated in the band of principal quantum number n. Ideally then, in terms of the Bloch functions $\psi_{n\vec{k}}$ for this band, one has

$$|n\rangle=\int_{BZ}a_{n\vec{k}}\psi_{n\vec{k}}(\vec{r})\,d\vec{k}\ . \qquad (36)$$

The coefficients, $a_{n\vec{k}}$, may be chosen such that the expectation value of the virtual orbital ϕ_{Aa} solving Eq. (10) is minimized. This prescription is reasonable, since the choice of virtual orbital in Eq. (10) has been shown to be variationally determined, and to possess a Koopmans's theorem for excita-

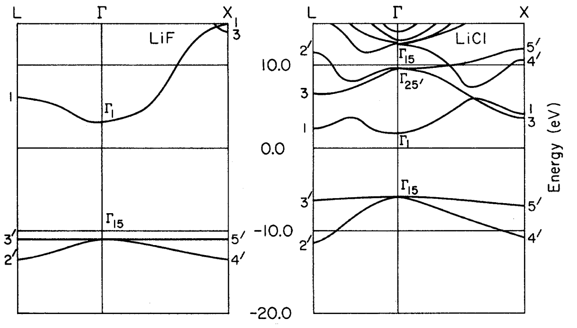

FIG. 2. Correlated energy bands for LiF and LiCl are given from Ref. 5.

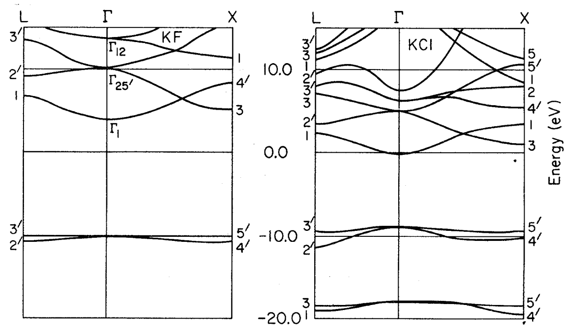

FIG. 4. Correlated energy bands for KF and KCl are given From Ref. 5.

TABLE II. Various contributions to the energy gaps are given for the rare-gas systems Ne and Ar. Correlation contribution is symbolized by $\Sigma^*(c)$, whereas the relaxation contribution is given as $\Sigma^*(r)$. Electron-hole interaction is essentially constant for all pair excitations on the Ne or Ar atoms. For excitations to the $3s$ level we deduce the value of K to be 3.45 ± 0.1 eV, and for excitations to the Ar $4s$ level K is found to be 1.5 eV. Results in eV.

Level	$\Sigma^*(c)$	$\Sigma^*(r)$
$1s$ Ne	1.08	22.89
$2s$ Ne	1.08	2.86
$2p$ Ne	1.08	2.95
Conduction-band Ne	−1.85	~0
$3p$ Ar	1.58	1.29
Conduction-band Ar	−1.67	~0

tions of the N-body system.[16,19] Therefore the shape of hole which optimizes the energy of ϕ_{Aa} also optimizes the excited-state total energy. This of course neglects relaxation of core-orbital's shape and correlation. These effects here are treated separately.

In practice, for the case of nonoverlapping orbitals (i.e., the orbitals for core states in this calculation), the proper choice of $|n\rangle$ for use in Eq. (10) is found to be the local orbital ϕ_{An} for the hole vacated. For simplicity, the author also uses this approximately for the case of valence excitations. Here, of course, overlap considerations dictate that this choice of $|n\rangle$ is not optimal. However, here the overlaps are small (of the order of 0.05 or less) and this should not be a significant problem. The calculations are performed using the same code as is used in solving for the local orbitals for the gorund state. Two shells of neighboring atoms are included in the calculation, and the remainder of the lattice is treated by a point ion model. This seems reasonable, in that the first excited levels for the cations or rare-gas atoms lie mostly inside the first-neighbor distance when $\hat{O}\hat{A}\hat{O}$ as described here is used. The value of K_{na} is then obtained by solving Eq. (10) with $\hat{A}$ in $\hat{O}\hat{A}\hat{O}$ set to zero and by taking the difference of the expectation value for ϵ_{Aa} in these two limits.

In practice one could also obtain the value of K_{na} for the anion excitations by this model. However, the duffuseness of the first excited level requires that one use a more varied angular basis set than the author is able to provide at this time in order to have an accurate estimate of the energy. Therefore, it is simple and about as accurate in this

TABLE III. Self-energies and the electron-hole interactions are given for LiF and LiCl. Results are in eV.

Level	System	$\Sigma^*(c)$	$\Sigma^*(r)$	K_{ia}
Li $1s$	LiF	2.92	1.52	−10.38
F $1s$	LiF	1.79	24.75	−3.74
F $2s$	LiF	1.79	4.00	−3.74
F $2p$	LiF	1.79	3.56	−3.74
Li $1s$	LiCl	2.45	1.52	−10.38
Cl $1s$	LiCl	2.42	33.44	−2.04
Cl $2s$	LiCl	2.42	11.51	−2.04
Cl $2p$	LiCl	2.42	12.54	−2.04
Cl $3s$	LiCl	2.42	1.99	−2.04
Cl $3p$	LiCl	2.42	1.48	−2.04
Conduction band	LiF	−2.38	−1.0	
Conduction band	LiCl	−1.61	···	

TABLE IV. Self-energies and the electron-hole interactions are given for NaF and NaCl. Results are in eV.

Level	System	$\Sigma^*(c)$	$\Sigma^*(r)$	K_{ia}
Na $1s$	NaF	2.13	22.70	−8.60
Na $2s$	NaF	2.13	2.79	−8.60
Na $2p$	NaF	2.13	3.10	−8.60
F $1s$	NaF	1.99	24.75	−3.59
F $2s$	NaF	1.99	4.00	−3.59
F $2p$	NaF	1.99	3.56	−3.59
Na $1s$	NaCl	2.43	22.70	−8.60
Na $2s$	NaCl	2.43	2.79	−8.60
Na $2p$	NaCl	2.43	3.10	−8.60
Cl $1s$	NaCl	1.31	33.41	−2.28
Cl $2s$	NaCl	1.31	11.51	−2.28
Cl $2p$	NaCl	1.31	12.54	−2.28
Cl $3s$	NaCl	1.31	1.99	−2.28
Cl $3p$	NaCl	1.31	1.48	−2.28
Conduction band	NaF	−1.11	···	
Conduction band	NaCl	−2.16	···	

TABLE V. Self-energies and the electron-hole interaction strength are given for KF and KCl. Results are in eV.

Level	Substance	$\Sigma^*(c)$	$\Sigma^*(r)$	K_{ia}
$1s$ K	KF	1.75	32.14	−7.22
$2s$ K	KF	1.75	9.98	−7.15
$2p$ K	KF	1.75	11.21	−7.13
$3s$ K	KF	1.75	1.36	−7.00
$3p$ K	KF	1.75	1.20	−6.84
$1s$ F	KF	1.93	24.75	−2.93
$2s$ F	KF	1.93	4.00	−2.93
$2p$ F	KF	1.93	3.56	−2.93
$1s$ K	KCl	1.96	32.14	−7.22
$2s$ K	KCl	1.96	9.98	−7.15
$2p$ K	KCl	1.96	11.21	−7.13
$3s$ K	KCl	1.96	1.36	−7.00
$3p$ K	KCl	1.96	1.20	−6.84
$1s$ Cl	KCl	1.06	33.14	−2.16
$2s$ Cl	KCl	1.06	11.51	−2.16
$2p$ Cl	KCl	1.06	12.54	−2.16
$3s$ Cl	KCl	1.06	1.99	−2.16
$3p$ Cl	KCl	1.06	1.48	−2.16
Conduction band	KF	−1.14	···	
Conduction band	KCl	−1.99	···	

TABLE VI. Theoretical band gaps are given for Ne (solid) in the Hartree-Fock and the correlated limit. Lower limit to exciton excitation is also given by subtracting K_{ij} from the corrected band gap. eV are used. Relativistic corrections are included in correlated results. ESCA energies are obtained by subtracting 9.64 eV from the correlated band gap. The Hartree-Fock data is from Ref. 5.

Gap	Hartree-Fock	Correlated	Excitonic
2*p*	25.15	19.27	15.82
2*s*	54.94	48.95	45.50
1*s*	900.46	872.98	869.53

case to use Eq. (33) to determine K_{na}. In this case $\vec{R}_A - \vec{R}_c$ is the nearest-neighbor distance. The author has tested this approximation on several molecules for which he is able to provide accurate calculations of charge transfer type excitations or core states. He finds the use of (33) introduces an error of about 20% in the value of K_{ia}. In the test cases the value of K_{ia} given by (33) was too large and thus in no way compromises the conclusion of this manuscript.

The basis set for the solid-state calculations consisted of *s*-, *p*-, and *d*-type Slater orbitals. The same basis set used for the local orbitals calculations of the ground state was employed, and was augmented by four additional diffuse *s*-type orbitals for describing the excited state (note symmetry prevents mixing of *p* or *d* orbitals in the excited state). The orbitals were even tempered in these calculations. In sum then for all 1*s* excitons the one-band-one-site model is used as is the effective-mass theory for all 2*p* excitons. For excitations of cation or rare-gas atom, the $\hat{O}\hat{A}\hat{O}$ theory is used to compute K_{ia} and Eq. (33) is used for anion excitation.

Band structures for substances Ne, Ar, LiF, NaF, KF, LiCl, NaCl, and KCl are shown in Figs. 1–4. These bands are obtained by starting with the self-consistent Hartree-Fock results in the literature.[5] To these results Σ^* is added. Σ^* here includes both correlation and relaxation. This had not been reported except for LiF. In addition, the bands for NaCl and KCl are corrected for the convergence of the plane-wave basis. (This is needed only for the 3*p* valence bands.) This correction was computed by the author by computing the Γ point in a self-consistent linear combination of atomic orbitals (LCAO) model.

TABLE VII. Fundamental band gap in Ar is studied. Calculated exciton gap is given also. eV are used. ESCA energies (with respect to the Fermi level) are obtained by subtracting 6.98 eV from the correlated gap. Hartree-Fock data is from Ref. 5.

Gap	Hartree-Fock	Correlated	Excitonic
3*p*	18.49	13.95	12.85

TABLE VIII. Band gaps for LiF are given. Correlated gaps include relativistic corrections. Minimum exciton gap is also given eV are used. ESCA levels with respect to the Fermi level) are found by subtracting 7.07 eV from the correlated gap. Hartree-Fock data is from Ref. 5.

Gap	Hartree-Fock	Correlated	Exciton
Li 1*s*	72.19	64.37	53.99
F 1*s*	724.04	695.29	691.55
F 2*s*	50.44	41.42	37.60
F 2*p*	22.96	14.13, 14.20	10.49

In addition to this, the values deduced by actual calculation for the values of the constitutents of Σ^* and for the K_{ij}'s for the various crystals studied are given in Tables II–V. From these tables one can deduce the great difference between the K's for on-site excitation and for charge tranfer excitation. In addition, one can see quite quickly for deep excitations the great dominance of the relaxation terms in determining the edge positions.

VI. COMPARISON OF RESULTS AND EXPERIMENT

The author has no wish to attempt a detailed comparison of experiment in the sense of writing one for each of the eight compounds considered independently. Instead the charts and figures enclosed here provide an adequate summary of the results as they stand with respect to the experimental situation. In Tables VI–XIII, the author provides for Ne, Ar, LiF, LiCl, NaF, NaCl, KF, KCl, respectively, a chart giving the Hartree-Fock band gaps, the corrected band gaps, the minimum exciton band gap, the minimum band gap for the 2*p* exciton if the 1*s* exciton would be a forbidden transition, the actual computed 1*s* exciton position from the Koster-Slater mod-

TABLE IX. Band gaps for LiCl are given. Correlated gaps include relativistic corrections. Minimum exciton gaps are given. ESCA levels (with respect to the Fermi level) are found by subtracting 3.85 eV from the correlated gap. Hartree-Fock data is from Ref. 5.

Gap	Hartree-Fock	Correlated	Exciton
Li 1*s*	70.21	63.63	53.25
Cl 1*s*	2857.47	2834.52	2832.48
Cl 2*s*	291.17	278.29	276.25
Cl 2*p*	221.97	205.81, 207.65	203.77
Cl 3*s*	35.03	29.33	27.29
Cl 3*p*	13.15	7.69, 7.83	5.65

TABLE X. Band gaps for NaF are given. Correlated gaps include relativistic effects. Minimum exciton gaps are given. Results are in eV. ESCA levels are obtained (with respect to the Fermi level) by subtracting 6.71 eV from the correlated gap.

Gap	Hartree-Fock	Correlated	Exciton
$1s$ Ni	1104.46	1081.11	1072.51
$2s$ Na	78.45	72.80	64.20
$2p$ Na	43.22	36.18, 36.39	27.58
$1s$ F	720.99	694.31	690.72
$2s$ F	46.42	39.47	35.88
$2p$ F	20.10	13.41, 13.44	9.82

TABLE XII. Band gaps of KF are given. Correlated gaps include relativistic corrections. Results are in eV. Minimum exciton gap is given. ESCA levels (with respect to the Fermi level) are found by subtracting 7.00 eV from the correlated gap.

Gap	Hartree-Fock	Correlated	Exciton
F $1s$	719.62	692.97	690.04
F $2s$	45.35	38.43	35.50
F $2p$	20.65	13.99, 14.07	11.06
K $1s$	3634.99	3622.73	3615.51
K $2s$	398.85	389.17	382.02
K $2p$	315.67	302.22, 305.31	295.09
K $3s$	50.35	46.72	39.72
K $3p$	28.13	24.15, 24.46	17.31

el, and finally, the theoretical ESCA energy is given. This is given, as is customary, with respect to the Fermi energy (assumed to be the middle of the optical band band gap). From these tables the reader is free to compute the difference in energy between occupied states based upon different processes. As previously noted, the difference due to the small atomic effects are ignored because they are small compared to charge transfer effects and also, because of the arbitrary nature of the effect breakup in the solid case, the small numbers are somewhat uncertain. It is unfortunate that the style of calculation employed for the atoms is impractical here, so these small effects are unavailable. Nonetheless, the reader should be aware of their existence.

The relationship to optical or soft-x-ray spectra is seen in Figs. 5–12 for Ne, Ar, LiF, LiCl, NaF, NaCl, KF, KCl, respectively. In these figures, the available spectra for each edge are shown. Also shown is the state density for the conduction band. Here the 0 of energy is set at the minimum of the conduction band, and the experimental spectra are shown so that this 0 lies at the position of the band gap given in Tables VI–XIII. In addition, the minimum positions for the $n=1$ and $n=2$ excitons are shown for each level as are the computed $n=1$ exciton positions. In general, one sees from such figures that it is possible to construct a satisfactory picture of the absorption process from this calculation. Explicit references to the experimental papers are given in the figure captions.

We will now take up a brief discussion of the relevant experimental data for the eight systems considered here and compare it with the present predictions.

a. Solid Ne. In the case of solid Ne, absorption begins with a series of sharp absorption peaks beginning at about 17.2 eV and terminating in a series limit at about 21.5 eV. Presumably the first peak is excitonic, and the series limit corresponds to the band gap. This theory predicts a value of 15.8 eV for the exciton absorption and 19.3 eV for the band gap. If this assignment is acceptable, the error is about 10%. A second series of absorptions from the $2s$ Ne level is seen to lie at 47.0 eV, with perhaps a series limit at about 48.5 eV. The theory predicts a forbidden exciton at 45.5 eV and an optically-allowed exciton ($2p$ like) at 48.0 eV, with a series limit or band gap of 49.0 eV. In this case

TABLE XI. Band gaps and minimum exciton gaps of NaCl are given. Results are in eV, and the correlated gaps include relativistic corrections. ESCA levels (with respect to the Fermi level) are given by subtracting 4.61 eV from the correlated gap. Hartree-Fock data is from Ref. 5.

Gap	Hartree-Fock	Correlated	Exciton
Na $1s$	1103.45	1079.05	1070.45
Na $2s$	76.42	69.08	60.48
Na $2p$	41.86	34.10, 34.21	25.50
Cl $1s$	2855.45	2833.08	2830.81
Cl $2s$	288.95	276.63	274.35
Cl $2p$	219.85	204.25, 206.09	201.97
Cl $3s$	31.61	26.99	24.71
Cl $3p$	14.12	9.22, 9.36	6.94

TABLE XIII. Band and minimum exciton gaps are given for KCl. Correlated gaps include relativistic corrections. Results are in eV. ESCA levels (with respect to the Fermi level) are given by subtracting 4.66 eV from the correlated gap. Hartree-Fock data is from Ref. 5.

Gap	Hartree-Fock	Correlated	Exciton
Cl $1s$	2853.61	2831.34	2829.78
Cl $2s$	289.33	277.43	275.27
Cl $2p$	220.38	205.20, 207.04	203.04
Cl $3s$	30.73	26.02	23.86
Cl $3p$	13.80	9.32, 9.46	7.16
K $1s$	3632.89	3613.49	3606.27
K $2s$	394.18	383.44	376.29
K $2p$	313.40	298.89, 301.98	291.76
K $3s$	47.51	42.82	35.82
K $3p$	23.09	18.05, 18.36	11.21

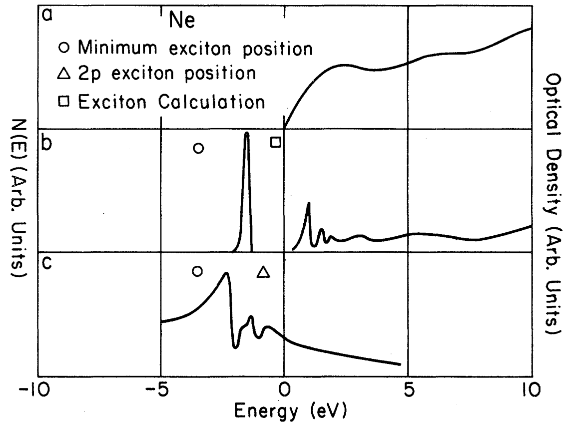

FIG. 5. (a) Density of states of the Ne conduction band; (b) absorption from the Ne $2p$ shell (Ref. 36); (c) absorption from the Ne $2s$ (Ref. 37). Energy zero is the computed band gap in Table VI.

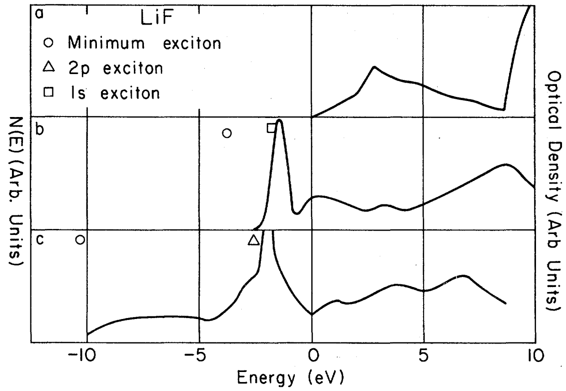

FIG. 7. (a) LiF conduction-band state density; (b) absorption from the F^- $2p$ level (Ref. 40); (c) absorption from the Li^+ $1s$ level (Ref. 2). Energy zero is the band edges in Table VIII.

the theory is consistent with experiment with an error of about 2%. The experimental data is from Refs. 36 and 37.

b. *Solid* Ar. For solid Ar, the fundamental optical absorption is found to begin with a sharp absorption peak lying at about 11.7 eV and is followed by further absorptions terminating in a series limit at about 14.0 eV. In the present calculation, we predict excitonic absorption to be at 12.8 eV and the band gap to lie at 14.0 eV. The theory and experiment are consistent. The data are taken from Ref. 39.

c. LiF. We have already discussed the case of LiF in the introduction. In this system, absorption from the valence band occurs at about 12.2 eV in an excitonic transition, with a series limit at perhaps[40] 13.6 eV or possibly alternately at about

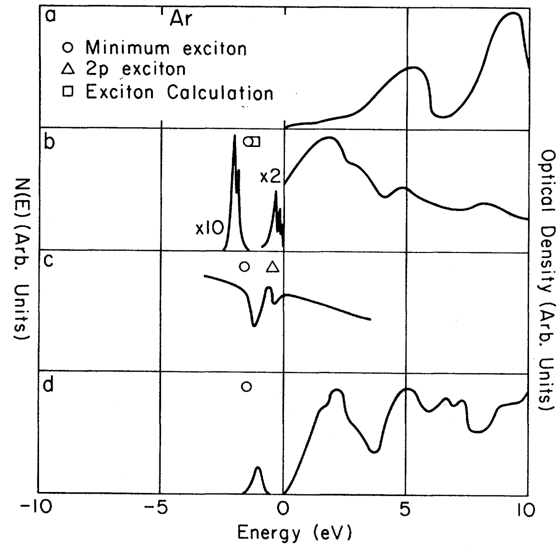

FIG. 6. (a) Density of states of the Ar conduction band; (b) absorption from the $3p$ level (Ref. 38); (c) absorption from the $3s$ level (Ref. 37); (d) absorption from the $2p$ level (Ref. 39). Zero of energy is the computed band gap in Table VII.

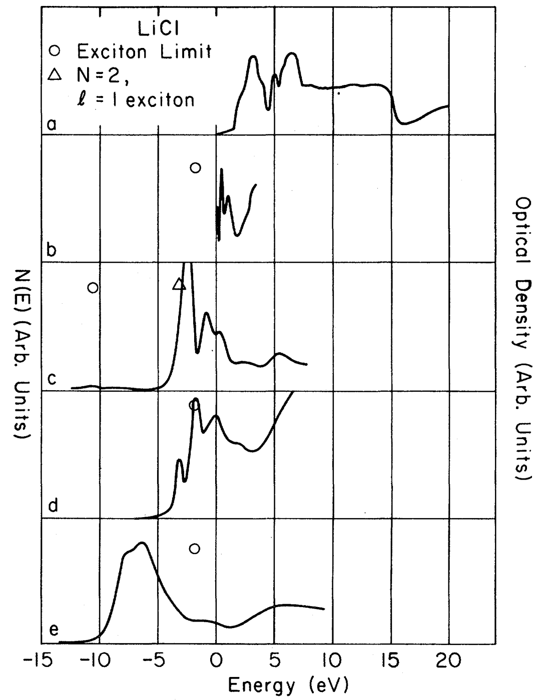

FIG. 8. (a) LiCl conduction-band density of states; (b) absorption from the Cl^- $3p$ level (Ref. 41); (c) absorption from the Li^+ $1s$ level (Ref. 42); (d) absorption from the Cl^- $2p$ level; (e) absorption from the Cl^- $1s$ level (Ref. 43). Zero of energy is the band gaps given in Table IX.

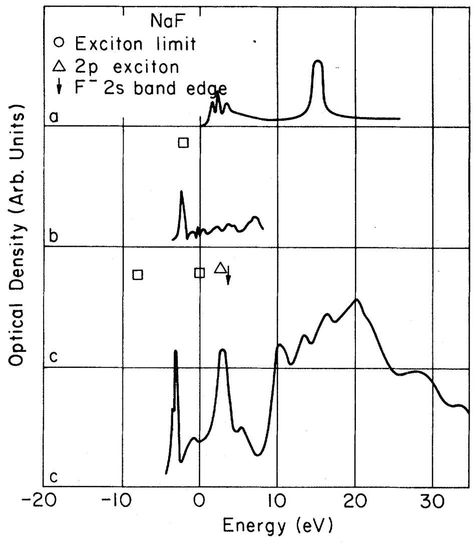

FIG. 9. (a) NaF conduction-band density of states; (b) absorption from the F$^-$ $2p$ level (Ref. 41); (c) absorption from the Na$^+$ $2p$ level (Ref. 43). Zero of energy is the band edge in Table X.

15.0 eV. The theory predicts an excitonic transition at 12.1 eV and a band gap of 14.2 eV. This is consistent with the proposed experimental interpretations. In the case of absorption from the Li 1s level, absorption begins at about 54 eV, has a sharp peak at about 62 eV, which may be excitonic, and a series limit of 64.4 eV. This theory predicts the lower limit for exciton absorption to be 54 eV with a forbidden transition, and an allowed $2p$ level exciton to lie at 61.8 eV with a series limit of 64.4 eV. This is quite consistent with the data and as discussed in the Introduction; the ESCA data which predicts an effective electron-hole interaction strength differences of about 10 eV for anion and cation excitation. The data are from Refs. 2 and 40. The neglect of neighbor relaxation, as discussed previously, suggests that the theoretical band gaps should be greater than the experimental ones for these narrow-band materials making the 13.6 experimental value more likely.

d. LiCl. The situation for LiCl is rather more complete and possibly more complicated than for the other salts considered here. The chief interest centers around the Li$^+$ 1s absorption edge. Briefly, the valence absorption is seen to start at about 7.7 eV with no well-defined series limit for exciton absorption. This may be due to the large dielectric constant of LiCl coupled with unusual conduction-band topologies creating an exciton of only a few meV binding.[5] The theoretical band gap here is 7.69 eV and the lower limit for exciton activity is 5.65 eV. In the case of the Li$^+$ 1s absorption, the onset may lie in a very weak peak at about 53.0 eV which in this calculation corresponds to a 1s exciton (optically forbidden) of energy 53.25 eV. A strong peak is seen at about 61 eV which corresponds to the calculated $2p$ exciton (optically allowed) of about 60.7 eV. The band gap is not seen here experimentally. However, the theory predicts a band gap of 63.6 eV. The case of absorption from the Cl$^-$ $2p$ shell and 1s shell are of a similar nature, with the theory predicting that the absorption onset is excitonic on obtaining perhaps realistic values for the band gap, as seen from Fig. 8 and Table IX. There is one point of interest, and this concerns the apparently greater strength of the exciton binding in the 1s or $2p$ Cl$^-$ absorption compared to the $3p$ level. This may be an artifact of the calculation due to the approximate nature of the inclusion of relativistic effects, or may reflect the stronger crystal charge rearrangement due to the formation of deep core holes. The data are from Refs. 41–43.

e. NaF. Data for NaF is available for absorption from the F$^-$ $2p$ level and the Na$^+$ $2p$ level. In the case of the F$^-$ $2p$ level, optical absorption begins in a sharp peak at 9.8 eV and has a series limit of about 13 eV. The present theory predicts an ex-

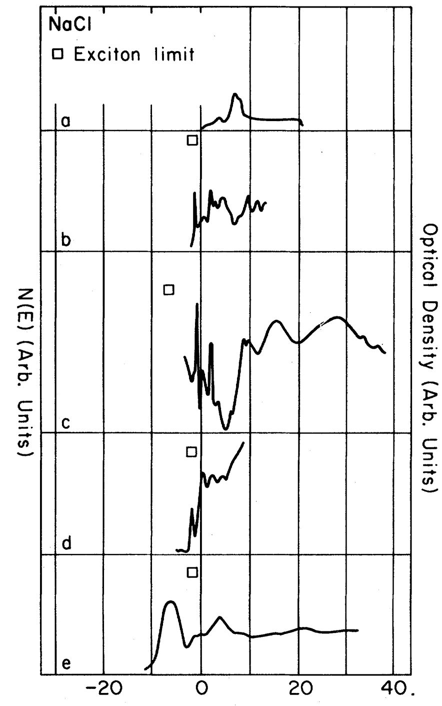

FIG. 10. (a) NaCl conduction-band density of states; (b) absorption from the Cl$^-$ $3p$ level (Ref. 47); (c) absorption from the Na$^+$ $2p$ level (Ref. 43); (d) absorption from the Cl$^-$ $2p$ level (Ref. 43); (e) absorption from the Cl$^-$ 1s level (Ref. 43). Energy zero is the computed band edge in Table XI.

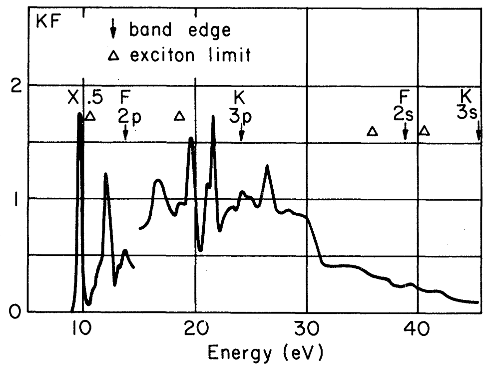

FIG. 11. Optical absorption of KF is shown here along with computed edges (Ref. 1).

citon to be at 9.8 eV and an optical band gap of 13.4 eV. In the case of the $2p$ F$^-$ level, the absorption onset lies at about 32 eV with a series limit at perhaps 36 eV, and with a further strong-absorption peak at 39 eV. The present theory predicts the Na$^+$ $2p$ gap to be 36.2 eV with a lower limit for exciton activity of 27.6 eV, a F$^-$ $2s$ band gap of 39.5 eV with a lower limit for exciton activity of 35.9 eV, and an allowed $2p$ exciton of 39.0 eV. Therefore, the authors suggest that the absorption peak at 39 eV is an exciton absorption associated with the F$^-$ $2s$ level rather than some state density feature associated with absorption from the Na$^+$ $2p$ shell to the conduction band. Here one clearly sees the cation has much stronger strength for exciton binding than the anion. The data used is from Refs. 41 and 43.

f. NaCl. As seen in Fig. 10 and Table XI, the situation for NaCl is quite similar to that for LiCl except that the valence exciton seems better bound experimentally for NaCl than for LiCl, no doubt reflecting on the lower dielectric constant of NaCl. Other than this the comments made for LiCl apply here.

g. KF. The case of KF is perhaps the most interesting in that relatively little prior effort has been made in interpreting the optical data for this substance. The optical-absorption data is seen in Fig. 11 and is due to Stephan.[1] In the range of energy studied experimentally, the present calculation finds four band edges. These are the F$^-$ $2p$ edge at 14.0 eV along with its exciton limit of 11.1 eV; the K$^+$ $3p$ edge at 24.15 eV along with its exciton limit of 17.3 eV; the F$^-$ $2s$ edge at 38.4 eV and its exciton limit of 35.5 eV; and the K$^+$ $3s$ edge at 46.7 eV along with its exciton limit of 39.7 eV. The author therefore proposes that the sharp observed absorption in KF at 9.5 and 13 eV are excitons associated with F$^-$ $2p$ absorption, and the dip at 13.5 eV is the band edge for the $2p$ F$^-$ level. It is further suggested that the K$^+$ $3p$ band edge is probably the observed minimum at 22.5 eV or possibly that at 24 eV, while the sharp absorptions at about 19 eV and 22 eV may well be excitons associated with the K$^+$ $3p$ state. As for both $2s$ levels there is an absence of pronounced structure in the experiments in the theoretical energy range and thus any attempt at definite assignments of structures seems futile.

h. KCl. KCl is quite similar in its complexity to the case of KF and, even though much effort has been expended upon KCl, the effort largely is concerned with the lowest absorption edge. The theory predicts a Cl$^-$ $3p$ band edge at 9.3 eV with an exciton limit of 7.16 eV, and a K$^+$ $3p$ band edge at 18.05 eV with an exciton limit of 11.21 eV; a Cl$^-$ $3s$ band edge at 26.0 eV with an exciton limit of 23.9 eV, and a K$^+$ $3s$ edge at 42.8 eV and an exciton limit of 35.8 eV. Experimentally one had sharp structure normally identified as excitons at 7.2 and 9.3 eV. If the band edge corresponds to the observed dip at 8.4 eV, then presumably the peak at 9.3 eV may still be identified to an exciton associated with the *d* conduction states, as is conventionally done. However, if the band edge lies at about 10.0–10.5 eV, as is also possible, then the peak at 9.3 eV may be a conventional exciton below the band gap. The present calculation slightly favors this latter possibility. The sharp peak at 11.2 eV amy be an exciton associated with the K$^+$ $3p$ level, and the valley at 17.5 eV may be its band edge. It is further possible that the weak peak at 26 eV is the exciton associated with the Cl$^-$ $3p$ level. A lack of sharp feature makes further assignments in this spectral range quite speculative.

In any event, the present theory provides a reasonable explanation of band and exciton edges for a wide range of materials and energy ranges. Further ESCA studies to further pin down the energies of band edges and exciton binding energies are greatly needed.

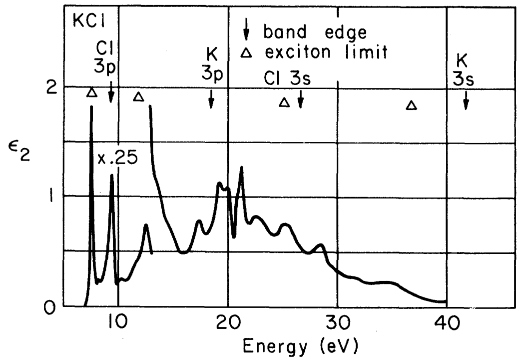

FIG. 12. Optical absorption of KCl is shown along with computed edges (Ref. 1).

VII. CONCLUSIONS

It has been shown that a satisfactory theory of soft-x-ray absorption in its gross features in insulators based upon a corrected Hartree-Fock band theory can be constructed. These corrections include correlation, relaxation, and electron-hole attraction. The correlation corrections are reasonably constant for all levels, whereas the relaxation terms increase markedly in importance with the deeper levels. They are never negligible. The Coulomb term for electron-hole interaction is relatively level-indenpendent for a given atom or ion (to within 1 eV as seen from the atomic study and also from $\hat{O}\hat{A}\hat{O}$ calculations for the other solid systems), but depend markedly on the type of atom or ion excited. The potentially smallest corrections are the exciting anions, the greatest for exciting cations, with neutral atoms having corrections intermediate in size. Also seen is the fact that the experimental determination of the separation of occupied levels is dependent upon the type of experiment. An explanation of this effect has been constructed which seems to have some quantitative accuracy.

It is useful to note the general trend to qualitative agreement for the importance of relaxation energy with increasing binding energy for the core states with a quite dissimilar type of calculation for the polaron.[44] It is also found for the polaron case that the greater the binding of the electron, the greater the tendency one has for a highly relaxed excited state. In this case, of course, one refers to ionic relaxation as well as presumably electronic relaxation. It is also useful to note that a successful employment of the relaxation term in Eq. (10) has been made for atomic Li calculations.[45] It seems likely that such a direct approach would be of great value for studies of solid-state systems when such a level of detailed precision is needed.

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of magnitude greater at the central site that for even the nearest neighbor in most cases, therefore justifying, in this case, the approximation.

[32] In addition to the smallness of the virtual state relaxation in this atom in a field limit, one has the relaxation being further diminished in a solid due to overlap corrections which diffuse the virtual state even more. This is often a good reason to neglect this effect entirely for excited electron. In LiF, however, even for excited levels this correction is small, but so are the overlaps, so that the retention if unnecessary is reasonable. The excited overlaps for the other crystals considered are rather larger than for LiF.

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