PHYSICAL REVIEW VOLUME 151, NUMBER 2 11 NOVEMBER 1966

Influence of Electronic Polarization on the Optical Properties of Insulators*

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(Received 8 April 1966)

The Toyozawa theory of the *electronic* polaron and the related Haken-Schottky theory of the optical dielectric function are applied to the alkali and silver halides and to the rare-gas solids. It is found that for most of these crystals the above dynamical theories reduce to a static limit. This in turn indicates that calculations of polarization effects based on the classical approach of Mott and Littleton will be valid. Such calculations are carried out in this paper. It is found that the self-energies due to the interaction of "bare" electrons or holes with the polarization field may be as large as several eV. Furthermore, because of the "inertialess" nature of electronic polarization, these self-energies and other polarization effects must be taken into account in the calculation of states which may be excited optically. Thus, for example, the optical band gap of certain alkali or silver halides may be as much as 5 eV smaller than a "good" one-electron band-structure calculation would yield. The available experimental data on the values of optical band gaps are critically reviewed and comparisons are made with the results of band-structure calculations. The computed r dependence of the optical dielectric function indicates that for small-radius excitations (e.g., $n=1$ excitons in many substances) electronic polarization should not influence the excitation energy in an important way; the electron and hole are "bare" particles when in the same unit cell. This fact is consistent with the success of a number of calculations in which polarization has been neglected. It is shown how the polarization dependence of the binding energies of these excitations can arise from the self-energies of the conduction electron and the valence-band hole. The use of the effective-mass method for computing binding energies is briefly discussed.

I. INTRODUCTION

We examine two basic (and related) questions which involve many-electron phenomena associated with optical absorption in insulating crystals[1–3]: (1) What is the relationship between an optical band-to-band energy—that is, the photon energy required to take an electron from a filled valence band and place it into an empty conduction band—and the corresponding energy that one might obtain in an accurate "one-electron" band-structure calculation? This question is pertinent in view of recent and current calculations of rare-gas[4–7] and alkali[8,9] and silver[10,11] halide band structures and comparisons of the results with optical data. (2) How are the binding energies of small-radius excitations (excitons or excited impurity states) related to the dielectric properties of the crystal?[12] Here the binding energy is as usual defined as the difference between the energy required to place an electron into the conduction band and that required to create the excitation, from a given ground state.

These problems are closely tied to the problem of the electronic polaron, that quasiparticle which consists of an electron or hole together with its associated electronic polarization.[13] Because this polarization is largely "inertialess" it affects transport properties but little; however, this same property means that electronic polarization must in general be included in calculations of excitations which may be optically created.

Section II contains a discussion of how electronic polarization manifests itself, both by introducing an r-dependent optical dielectric function[12] into the electron-hole interaction and by contributing self-energy, or polarization energy,[13] corrections to the one-electron energies. It is shown that for many insulators Toyozawa's[13] theory of the electronic polaron reduces to a static approximation. This indicates that a treatment of polarization energies of the type first given by Mott and Littleton[14] should be valid; we give a tabulation of the static self-energies for a number of insulating crystals. The Haken-Schottky theory[12] of the dielectric function also reduces to a "static" theory. After critically reviewing the experimental data on optical band gaps in rare gases and alkali and silver halides, we compare several computed band gaps with experiment.

In Sec. III we discuss how these considerations might affect the binding energies of small-radius excitations.

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* This research was supported in part by the Advanced Research Projects Agency under Contract SD-131 and by the U. S. Air Force Office of Scientific Research under Grant AF 803.

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[1] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963).

[2] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962).

[3] References 1 and 2 review much of the pertinent work through 1962–1963. Other and more recent work will be referred to throughout this paper.

[4] R. S. Knox and F. Bassani, Phys. Rev. **124**, 652 (1961).

[5] L. F. Mattheiss, Phys. Rev. **133**, A1399 (1964).

[6] W. Beall Fowler, Phys. Rev. **132**, 1591 (1963).

[7] M. H. Reilly, Ph.D. thesis, University of Rochester, 1966 (unpublished).

[8] P. DeCicco, Solid State and Molecular Theory Group, MIT Quarterly Progress Report No. 56, p. 49, 1965 (unpublished).

[9] D. Kahn and F. W. Quelle, Bull. Am. Phys. Soc. **10**, 347 (1965); S. Oyama and T. Miyakawa, J. Phys. Soc. Japan **21**, 868 (1966).

[10] F. Bassani, R. S. Knox, and W. Beall Fowler, Phys. Rev. **137**, A1217 (1965).

[11] P. Scop, Phys. Rev. **139**, A934 (1965).

[12] H. Haken and W. Schottky, Z. Physik Chem. **16**, 218 (1958).

[13] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **12**, 422 (1954).

[14] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

Use of the effective-mass method for these excitations in alkali and silver halides and rare gases is discussed. It is argued that a small-radius approximation for computing excitation energies is reasonably accurate for $n=1$ excitons in most of these crystals, although probably not for the silver halides. It is shown how the dependence of the binding energy on dielectric properties can arise from the self-energies of the "free" electron and hole.

Throughout this paper lattice polarization effects are neglected. These are not expected to be important in optical absorption for the systems considered.

II. THE EFFECTS OF CORRELATION: SELF-ENERGIES AND THE R-DEPENDENT DIELECTRIC FUNCTION

A. Historical Review

In the usual one-electron calculation, based upon Hartree-Fock theory, correlation (except as included in the Pauli principle) is neglected. Conduction-band electrons and valence-band holes are treated as "bare" particles moving through a sea of electrons and nuclei which do not respond to their presence, except possibly to their average position. Clearly this approximation cannot be correct, in general; one expects that the extra charge, especially if it is moving slowly, will polarize its surroundings to some extent. Just how much, and how this polarization will affect the electronic states, are questions which have stimulated much research.

Probably the first calculations of electron and hole polarization energies were made in the 1930's in attempts to interpret certain experimental data, including the ultraviolet absorption spectra of the alkali halides.[15] In these calculations the conduction electron and valence-band hole were treated as static point charges located on particular ions, and the energy associated with the electronic polarization of valence electrons on neighboring ions was calculated by methods of classical electrostatics, using empirical values of ionic polarizabilities, dielectric constants, and lattice constants. It was assumed that the frequency of the excited electron was sufficiently large that the lattice polarization could not change during the optical transition (the Franck-Condon principle), but electronic polarization was assumed to "follow" perfectly the excited electron.

With such assumptions Klemm[16] calculated the polarization energy of an electron and a hole one nearest-neighbor distance apart, while Mott and Littleton[14] developed a perturbation scheme for calculating the polarization energy of separated electrons and holes. The Mott-Littleton results have since been slightly modified by using both different ionic polarizabilities and different approximate methods of solution. Regardless of their quantitative accuracy, the classical values of electronic polarization energy should serve as upper limits to the true values, since allowing the extra particles to move would presumably decrease the magnitude of their polarization energies (in the limit in which the extra particles move very rapidly, there should be no response from the core electrons). A convenient limiting case for quantum-mechanical treatments is thus afforded.

It seems clear the validity of such a "static approximation" will be somewhat limited, in general, and a quantum-mechanical treatment is desirable. In 1954 Toyozawa[13] provided the first such treatment. Toyozawa considered the interaction of an extra particle (characterized by an effective mass) with the rest of the electrons, whose excitations were approximated by one band of virtual excitons of energy E_{ex}. He was able to formulate the problem so that it resembled the lattice polaron problem, with the virtual excitons replacing the virtual optical phonons and E_{ex} replacing $\hbar\omega$, the longitudinal-optical mode energy. He used intermediate-coupling theory[17] and obtained solutions formally similar to those of the lattice polaron problem.

Haken and Schottky[12] in 1958 took the results of Toyozawa and derived an expression for the interaction of an electron and a hole via electronic polarization. Their interaction included both an r-dependent dielectric function and self-energy corrections. The form of the resulting interaction was the same as that derived by Haken[18] for lattice polarization. Other calculations based upon these ideas have been reported by Weller[18a] and by Hanisch.[18b]

During this period there appeared a number of Russian papers[19] on band-structure calculations for an extra valence-band hole or conduction electron in alkali halides. The Russian workers included correlation in their calculations in a way which amounted to a refined Mott-Littleton approach. They assumed that the extra particle does not polarize the ion on which it is situated but that it interacts with the other ions as a classical charge distribution. Not surprisingly, the cor-

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[15] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, England, 1948), 2nd ed., reprinted by Dover Publications Inc., New York, 1964.

[16] W. Klemm, Z. Physik **82**, 529 (1933).

[17] T.-D. Lee, F. Low, and D. Pines, Phys. Rev. **90**, 297 (1953); M. Gurari, Phil. Mag. **44**, 329 (1953); S. V. Tiablikov, Zh. Eksperim. i Teor. Fiz. **22**, 325 (1952).

[18] H. Haken, in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963), p. 295.

[18a] W. Weller, Z. Naturforschg. **16a**, 401 (1961).

[18b] G. Hanisch, Phys. Kondens. Materie **4**, 297 (1965).

[19] T. I. Kucher, Zh. Eksperim. i Teor. Fiz. **34**, 394 (1958); **35**, 1049 (1958) [English transls.: Soviet Phys.—JETP **7**, 274 (1958); **8**, 732 (1958)]; T. I. Kucher and K. B. Tolpygo, Zh. Eksperim. i Teor. Fiz. **31**, 1002 (1956) [English transl.: Soviet Phys.—JETP **4**, 883 (1957)]; T. I. Kucher and K. B. Tolpygo, Fiz. Tver. Tela **2**, 2301 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2052 (1961)]; K. B. Tolpygo and O. F. Tomasevich, Fiz. Tver. Tela **2**, 3110 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2765 (1960)]; Z. Ya. Evseev and K. B. Tolpygo, Fiz. Tver. Tela **4**, 3644 (1962) [English transl.: Soviet Phys.—Solid State **4**, 2665 (1962)]; Z. Ya. Evseev, Fiz. Tver. Tela **5**, 2345 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1705 (1964)]; K. B. Tolpygo, in *Proceedings of the International Conference on Semiconductor Physics* (Publishing House of the Czechoslovak Academy of Science, Prague, 1961), p. 55.

rections to one-particle energies which they obtained are numerically close to those of Mott and Littleton.

The importance of correlation effects in semiconductors was also recognized. This problem was discussed by Kohn,[20] and relevant calculations have been performed by a number of others.[21–24] In these calculations the virtual states of polarization have been taken to be uncoupled electron-hole states.

In the case of semiconductors the observed breakdown of the effective-mass approximation for the lowest bound state associated with ionized impurities has led to investigations into the theory of r-dependent dielectric functions.[25] In some of the cases which we are considering (small-radius states in insulators) it has been *assumed* that the effective-mass approximation would not work well, even in zeroth order, and other types of zeroth-order calculations have been performed.

B. Calculations

1. The Classical Calculation

The basic classical problem is this: Given an extra point charge located on a particular ion and a set of polarizable ions, calculate the induced dipole moments on each ion due to both the extra charge and the induced moments on other ions. An exact solution is impossible, but adequate approximations can be made. Mott and Littleton[14] used perturbation theory to treat the problem for ionic crystals, while Rittner, Hutner, and DuPré[26,27] exactly solved a truncated set of simultaneous equations. The problem has also been treated by Kucher.[28]

We have computed the relevant energies in the first approximation of Mott and Littleton, using the ionic polarizabilities of both Pauling[29] and Tessman, Kahn, and Shockley.[30] The latter polarizabilities yield smaller electron self-energies, larger hole self-energies (by ≈ 0.1 eV) than the former, but the sum of electron and hole energies for a given crystal does not differ very much. These results are all within 0.2 eV of those given by DuPré *et al.*

TABLE I. Static electronic self-energies and damping parameters for an extra particle. For ionic crystals, $H_{se}(e)$ and $H_{se}(h)$ indicate that the particle is situated on a positive or a negative ion, respectively. For the rare gases the self-energies are equal in magnitude and refer to an extra particle on any atom. $2a$ equals the lattice constant, while K_0 is the optical dielectric constant. Except for CsF and the rare gases, the data and the self-energies are taken from Ref. 27. The damping parameters were computed from Eq. (10). For the rare gases the dielectric constants were estimated from the Clausius-Mossotti relation, using polarizabilities tabulated in Ref. 15. See also G. Baldini, Phys. Rev. 128, 1562 (1962).

	Data		Absolute values of self-energies (eV)			Damping parameters (Å^{-1})	
Substance	a(Å)	K_0	$H_{se}(e)$	$H_{se}(h)$	Sum	α_e	α_h
LiF	2.01	1.92	2.92	1.81	4.73	0.72	0.44
NaF	2.31	1.74	2.13	1.50	3.63	0.70	0.49
KF	2.67	1.85	1.75	1.66	3.41	0.53	0.50
RbF	2.82	1.93	1.64	1.76	3.40	0.47	0.51
CsF	3.00	2.19	1.61	2.14	3.75	0.42	0.55
LiCl	2.56	2.75	3.14	1.89	5.03	0.68	0.42
NaCl	2.81	2.25	2.43	1.53	3.96	0.60	0.38
KCl	3.14	2.13	1.96	1.42	3.38	0.51	0.37
RbCl	3.27	2.19	1.86	1.48	3.34	0.47	0.38
LiBr	2.74	3.16	3.18	1.91	5.09	0.65	0.39
NaBr	2.98	2.62	2.60	1.61	4.21	0.58	0.36
KBr	3.29	2.33	2.06	1.43	3.49	0.50	0.35
RbBr	3.43	2.33	1.91	1.44	3.35	0.46	0.35
LiI	3.00	3.80	3.17	1.89	5.06	0.60	0.36
NaI	3.23	2.91	2.57	1.57	4.14	0.54	0.33
KI	3.53	2.69	2.18	1.44	3.62	0.48	0.32
RbI	3.66	2.63	2.02	1.42	3.44	0.45	0.32
AgCl	2.77	4.01	3.12	2.55	5.67	0.58	0.47
AgBr	2.88	4.62	3.24	2.49	5.73	0.57	0.44
Ne	2.18	1.26	0.68	0.68	1.36	0.46	0.46
Ar	2.66	1.67	1.10	1.10	2.20	0.38	0.38
Kr	2.92	1.80	1.10	1.10	2.20	0.34	0.34
Xe	3.04	2.23	1.32	1.32	2.64	0.33	0.33

The self-energies computed by DuPré *et al.*[27] are given in Table I (except for CsF, which we computed using Mott and Littleton's first approximation and Pauling's polarizabilities). For the ionic crystals the hole is assumed localized on a negative ion, the electron on a positive ion. Also tabulated are results which we have obtained for the rare gases using Mott and Littleton's first approximation (for the purposes of this calculation the rare gases may be considered to be alkali halides with only one sublattice). In this table, $2a$ is the lattice constant, K_0 the optical dielectric constant.

The sign of these self-energies is such that the hole energy is raised and the electron energy lowered. Thus the difference between electron and hole energies is reduced by the sum of the absolute values of their self-energies.

2. Semicontinuum Calculation of F-Center Energies

In the well-known semicontinuum model[31,32] of the F center, self-energies and the r dependence of the di-

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[20] W. Kohn, in *Proceedings of the International Conference on Semiconductor Physics* (Publishing House of the Czechoslovak Academy of Science, Prague, 1961), p. 15.

[21] G. W. Pratt, Jr., Phys. Rev. **118**, 462 (1960).

[22] D. Penn, Phys. Rev. **128**, 2093 (1962).

[23] A. Morita, M. Azuma, and H. Nara, J. Phys. Soc. Japan **17**, 1570 (1962); Y. Abe, Y. Osaka, and A. Morita, *ibid.* **17**, 1576 (1962); M. Azuma, *ibid.* **18**, 194 (1963); **19**, 198 (1964); M. Azuma and K. Shindo, *ibid.* **19**, 424 (1964).

[24] M. H. Cohen and J. C. Phillips, Phys. Rev. **124**, 1818 (1961); M. H. Cohen, *ibid.* **130**, 1301 (1963).

[25] K. Müller, Solid State Commun. **2**, 205 (1964); Phys. Letters **14**, 299 (1964).

[26] E. S. Rittner, R. A. Hutner, and F. K. DuPré, J. Chem. Phys. **17**, 198 (1949); R. A. Hutner, E. S. Rittner, and F. K. Dupré, *ibid.* **17**, 204 (1949).

[27] F. K. Dupré, R. A. Hutner, and E. S. Rittner, J. Chem. Phys. **18**, 379 (1950).

[28] T. I. Kucher, Zh. Eksperim. i Teor. Fiz. **30**, 724 (1956); [English transl.: Soviet Phys.—JETP **3**, 580 (1956)].

[29] L. Pauling, Proc. Roy. Soc. (London) **A114**, 191 (1927).

[30] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[31] J. A. Krumhansl and N. Schwartz, Phys. Rev. **89**, 1154 (1953); see also the discussion by B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

[32] W. Beall Fowler, Phys. Rev. **135**, A1725 (1964).

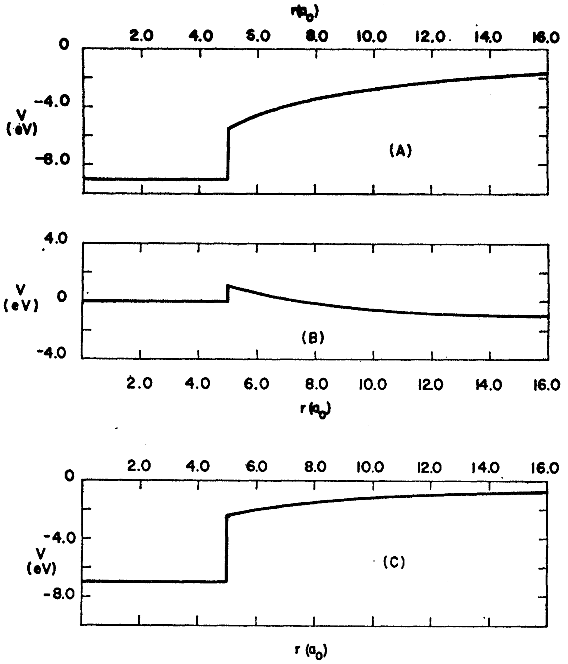

FIG. 1. Evolution of the F-center potential in the semicontinuum approximation. See text for details.

electric function *have* been taken into account in the static approximation, although the results have not generally been expressed in these terms. It seems instructive, therefore, to point out where these effects arise. A possible evolution of the potential in this model is shown in Fig. 1, where the numbers are pertinent to NaCl.[32] 1(a) represents a one-electron potential in which correlation effects have been neglected; there exists a potential well of depth E_M, the Madelung energy, and outside a distance R (the Mott-Littleton radius, approximately equal to the nearest-neighbor distance) the potential is $-e^2/r$. The zero of energy is taken to be the vacuum energy. This is not really correct, since in the effective-mass approximation the zero of energy should be the lowest point in the conduction band; also, correlation has not yet been included.

1(b) represents the sum of the corrections of these omissions. Inside the potential well these corrections are zero, while outside their sum is $(-e^2/2R)(1-1/K_0)-\chi+(e^2/r)(1-1/K_0)$. The first of these terms is the vacancy self-energy, discussed by Krumhansl and Schwartz.[31] It is just the Mott-Littleton energy, and for a vacancy the static approximation is probably quite good. χ is the experimental electron affinity (equal to ≈ 0.5 eV for NaCl) which automatically takes into account *both* the band structure effect and the self-energy of the electron. Finally, the last term introduces the optical dielectric constant for $r>R$. 1(c) represents the final potential, in which the zero of energy has been shifted to the bottom of the conduction band.

It should be noted that the net effect of the correlation plus band structure corrections is quite small for values of r up to $\approx 10\ a_0$. It is not surprising, then, that the energy difference between fairly localized states, like the $1s$ and the $2p$, is rather insensitive to these corrections,[2] and that different types of calculations yield similar results for their separation. One should note, of course, that for large r the correction becomes substantial, approaching ≈ 2 eV in this case.

3. The Theories of Toyozawa and of Haken and Schottky

We have just seen that for a system in which the "hole" is fixed (e.g., a vacancy) and for which the electron affinity is known empirically, it is possible to account for correlation effects in a fairly satisfactory way. But in the more general case it is of interest to know how good or bad the static approximation is. We thus turn to the result of Haken and Schottky, based on the electronic polaron theory of Toyozawa.[13] According to Haken and Schottky,[12] the interaction between the electron and hole is given by

$$H_I(r)=\frac{-e^2}{r}+\tfrac{1}{2}\sum_{\mathbf{k}}|\gamma_{\mathbf{k}}|^2 \times\left\{\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\hbar^2k^2/2m_e^*+E_{\mathrm{ex}}}+\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\hbar^2k^2/2m_h^*+E_{\mathrm{ex}}}+\mathrm{c.c.}\right\} +H_{\mathrm{se}}(e)+H_{\mathrm{se}}(h)\,, \quad (1)$$

where $\mathbf{k}$ is the wave vector, E_{ex} the exciton energy (the polarization is due to virtual excitons), r the electron-hole separation, and m_e^* and m_h^* are the effective masses of the two particles. c.c. stands for complex conjugate. $|\gamma_{\mathbf{k}}|^2$ is given by

$$|\gamma_{\mathbf{k}}|^2=(E_{\mathrm{ex}})^2(4\pi/Vk^2)(\alpha/u)\,, \quad (2)$$

where V is the crystal volume and α/u is given by

$$\alpha/u=(e^2/2E_{\mathrm{ex}})(1-1/K_0)\,. \quad (3)$$

The two H_{se} terms represent the self-energies of the electron and of the hole with respect to the electronic polarization. These self-energies are just those obtained by Toyozawa,[13] and are given by the second term in Eq. (1), with $\exp\pm(i\mathbf{k}\cdot\mathbf{r})$ replaced by -1.

We evaluate H_I by converting $(1/V)\sum_{\mathbf{k}}$ into $[1/(2\pi)^3]\int d^3k$, and integrate to $k=\pi/a$, where $2a$ is the lattice constant. We take the same k cutoff[33] as that used in the lattice polaron problem, and as we used in a calculation of lattice polarization effects for the F center.[32] π/a is approximately the Debye wave vector and is such that the correct number of exciton states is contained in one exciton band. If we write

$$v_i\equiv\left(\frac{2m_i^*E_{\mathrm{ex}}}{\hbar^2}\right)^{1/2}, \quad (4)$$

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[33] T.-D. Lee and D. Pines, Phys. Rev. 92, 883 (1953); T. D. Schultz, *ibid.* 116, 526 (1959).

then H_I becomes

$$H_I(r)=\frac{-e^2}{r}+e^2(1-1/K_0)\frac{1}{\pi}$$

$$\times\int_0^{\pi/a}\left[\frac{\sin kr}{kr}-1\right]dk\left[\frac{1}{1+k^2/v_e^2}+\frac{1}{1+k^2/v_h^2}\right]. \quad (5)$$

$(\sin kr)/kr$ introduces the r dependence, while the (-1) yields the self-energy.

Both parts of the integral depend in a critical way upon the relative size of v_i and π/a. If v_e and v_h are much smaller than π/a, one may replace the limit π/a by ∞ and obtain the Haken and Schottky result

$$H_I{}^{HS}(r)=\frac{-e^2}{r}+\frac{e^2}{r}(1-1/K_0)[1-\tfrac{1}{2}(e^{-v_er}+e^{-v_hr})]$$

$$\times\frac{-e^2}{2}\left(1-\frac{1}{K_0}\right)(v_e+v_h). \quad (6)$$

On the other hand, if v_i is much larger than π/a (for a vacancy or impurity $v_h=\infty$) the term in k^2/v_i^2 is negligible and the interaction becomes in the static limit

$$H_I{}^S(r)=\frac{-e^2}{r}+\frac{2e^2}{\pi r}\left(1-\frac{1}{K_0}\right)$$

$$\times\int_0^{\pi r/a}\frac{\sin x}{x}dx-\frac{2e^2}{a}\left(1-\frac{1}{K_0}\right). \quad (7)$$

An exponential fit to the Si integral yields

$$H_I{}^S(r)\approx\frac{-e^2}{r}+\frac{e^2}{r}\left(1-\frac{1}{K_0}\right)(1-e^{-2r/a})-\frac{2e^2}{a}\left(1-\frac{1}{K_0}\right). \quad (8)$$

This behaves properly as $r\rightarrow 0$ and as $r\rightarrow\infty$; it slightly underestimates the second term for $r\approx a$.

It is interesting to compare the self-energy $-e^2(1-1/K_0)(2/a)$ (the sum of electron and hole terms) obtained in the static limit of the Haken-Schottky theory with the Mott-Littleton result, $-e^2(1-1/K_0)[(1/2R_e)+(1/2R_h)]$. If R_e and R_h, the Mott-Littleton radii,[14] were both equal to $a/2$ there would be complete agreement; actually they generally turn out to be somewhat larger. It is not surprising that there is some disagreement since in a sense the Haken-Schottky theory in this limit is equivalent to a zero-order static approximation. Presumably the Mott-Littleton results are somewhat more reliable in this limit.

TABLE II. Comparison of the "exact" self-energy factor $v\tan^{-1}(\pi/a)/v$ with the static approximation, π/a, and the dynamic approximation, $\pi v/2$, for various values of v [Eq. (4)]. a is the nearest-neighbor distance in ionic crystals in units of a_0, while v is in units of $a_0{}^{-1}$.

π/a	m^*	E_{ex}(eV)	v	$\pi v/2$	$v\tan\frac{\pi/a}{v}$
0.53	4.0	8.0	1.5	2.4	0.51
0.53	1.0	8.0	0.77	1.2	0.47
0.53	0.5	8.0	0.53	0.83	0.42
0.47	0.2	6.3	0.31	0.48	0.31

We now examine how well either of these limits describes insulators. As a prototype alkali halide or rare gas,[1,14,34] we take $a=6a_0$, $E_{\text{ex}}=8$ eV. For holes in valence bands, m^* is expected to be large, say ≈ 4. For conduction electrons m^* is expected to be between 0.2 and 1. The larger values will probably obtain for alkali fluorides, chlorides, and bromides, and rare gases, while the smaller values may be pertinent to some alkali iodides and to the silver halides. We treat KI as a prototype of a small m^* case, using $a=6.65$ a_0, $E_{\text{ex}}=6.3$ eV, $m^*=0.2$.

The self-energy integral is proportional to $v_i\tan^{-1}\times[(\pi/a)/(v_i)]$. In the static limit this approaches π/a while in the dynamic limit it approaches $\pi v_i/2$. In Table II we indicate some values computed from the parameters listed above. For both the electron and the hole (except for the case $m^*=0.2$) the self-energy factor is much closer to the static limit (π/a) than to the dynamic limit $(\pi v_i/2)$, and in fact the dynamic limit yields a self-energy which is far too large. For $m^*=0.2$ the static and dynamic limits yield the same result, slightly larger than the "exact" result. The "exact" self-energy for KI is 1.68 eV; in the static and dynamic limits one obtains 2.55 eV, while the result of DuPré *et al.* (Table I) is 2.18 eV.

In a similar way, we find that the r dependence of H_I is much closer to the static than the dynamic result, for large-m^* insulators.

It is interesting to note that by the usual criterion these electronic polarons are rather weakly coupled, with α, the coupling constant, $\lesssim 1$. Lee and Pines[33] showed that for strong-coupling polarons a cutoff in the k integral was necessary; but even for these weak-coupling polarons such a cutoff is essential. (In fact, our "static" self-energy is entirely analogous to their strong-coupling result.) The small value of α is actually somewhat misleading; since the polaron self-energy (without the cutoff) is $\approx -\alpha E_{\text{ex}}$, the perturbation on the bare-state energy is quite large. This contrasts with the lattice polaron in these crystals, where $\alpha\approx 5$ but the longitudinal optical phonon energy is several orders of magnitude smaller than E_{ex}, so the self-energy is only ≈ -0.1 eV and the cutoff is not necessary.

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[34] See Ref. 32 for a discussion of the effective mass in alkali halides. Recently, M. Mikkor, K. Kanazawa, and F. C. Brown [Phys. Rev. Letters **15**, 489 (1965)] have found that the cyclotron effective mass for electrons in KBr is about 0.5, while J. Ramamurti and K. J. Teegarden [Phys. Rev. **145**, 698 (1966)] have inferred exciton reduced masses of 0.21 and 0.32 for KI and RbI, respectively. G. Baldini [Phys. Rev. **128**, 1562 (1962)] has obtained reduced exciton masses of order 0.5 for xenon and krypton. G. Ascarelli and F. C. Brown [Phys. Rev. Letters **9**, 209 (1962)] used cyclotron resonance and determined the effective mass of conduction electrons in AgBr to be ≈ 0.2.

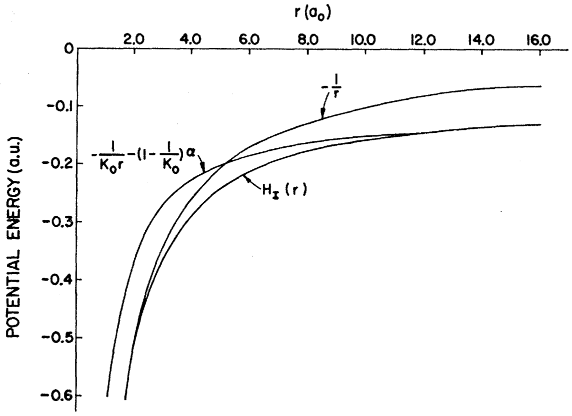

FIG. 2. The behavior of several potentials as a function of r. $H_I(r)$ is given by Eq. (9), with $\alpha_e=\alpha_h=2a_0^{-1}$ and $K_0=2.0$. Plotted also are a "bare" Coulomb potential $-1/r$ and a potential which contains a self-energy term plus a dielectrically shielded Coulomb term, $-(1-1/K_0)\alpha-1/K_0r$. (a.u.=atomic units.)

Having used the theory of Haken and Schottky to obtain the connection between the damping length in H_I and the self-energy, and having shown that the static approximation for calculating these quantities is valid in certain cases, we propose that a reasonable approach is to write an r-dependent potential as

$$H_I(r)=\frac{-e^2}{r}+\frac{e^2}{r}\left(1-\frac{1}{K_0}\right)\left[1-\tfrac{1}{2}(e^{-\alpha_e r}+e^{-\alpha_h r})\right]+H_{\rm se}(e)+H_{\rm se}(h), \quad (9)$$

compute the self-energies by the Mott-Littleton method, and determine the α's by the requirement that $H_I(r)$ approach $-e^2/r$ as r approaches zero. This yields

$$H_{\rm se}(i)=-(e^2/2)(1-1/K_0)\alpha_i. \quad (10)$$

The damping parameters α_i which correspond to the self-energies $H_{\rm se}(i)$ are listed in Table I.

Figure 2 illustrates the behavior of $H_I(r)$ [Eq. (9)] for a model case in which $\alpha_e=\alpha_h=0.2a_0^{-1}$ and $K_0=2.0$. Plotted also are a "bare" Coulomb potential $-1/r$ and the sum of the self-energy correction plus a Coulomb potential with dielectric constant, $-(1-1/K_0)\times\alpha-(1/K_0r)$. One can see how the "exact" potential approaches the other two for small and large r, respectively. It is also clear that a fairly good approximation is obtained by using $-1/r$ for $r<\alpha^{-1}$ and $-1/K_0r-(1-1/K_0)\alpha$ for $r>\alpha^{-1}$.

In general, the r dependence of the dielectric function will not be the *only* core correction of importance; for r small enough that polarization effects become small, other effects will certainly be important.[1] The F-center problem which we have discussed is a good example of a situation in which the potential energy does *not* go as $-e^2/r$ for small r.

The connection between α and $H_{\rm se}$ pointed out in Eq. (10) is important, for it helps provide a test of various theories of r-dependent dielectric functions. Azuma,[23] for example, has derived such a function for KCl as a sum of several exponentials. However, his constants are chosen so that the self-energy vanishes, which, according to our arguments, is not correct. In performing a calculation on solid rare gases, Hermanson[35] has taken α to be equal to the Fermi momentum, whose numerical value is of order 0.5 atomic units (a.u.) for these substances. This value of α leads to self-energies for electron plus hole of ≈ -7.5 eV, three times what a Mott-Littleton treatment would give (see Table I). Our arguments indicate that α should be more like 0.2 a.u. (or 0.33 Å^{-1}) for these crystals.

C. One-Electron and Optical Band Gaps

1. Self-Energy Corrections

We now argue that the numbers in the "sum" column of Table I represent the approximate self-energy corrections that should be subtracted from one-electron energy gaps to obtain optical gaps. This statement involves several assumptions. The first of these is that the Mott-Littleton type of approach is a valid one to use in computing these quantities. We have argued that this approach is valid, at least for the large-m^* substances. But even for the small-m^* substances such as KI and the silver halides, the numbers listed in Table I are not expected to overestimate the self-energies by more than ≈ 1 eV. As mentioned earlier, the tabulated value for KI is only ≈ 0.5 eV larger than the "exact" dynamical result. Better comparisons must await the further determination of effective masses for small-m^* substances. For any of these, however, the values given in Table I are probably not far from correct.

The second of these assumptions is that the states described above are those which will be directly populated by the absorption of photons. The omission of any consideration of lattice polarization indicates that we are making a strict Franck-Condon approximation, and that the lattice responds sufficiently slowly that the excited "electron-only" state is relatively stationary.[2] This approximation is common, although it neglects possible lattice polaron self-energy effects. But the self-energies of lattice polarons[17] are typically rather small (≈ -0.2 eV) in comparison with electronic polaron self-energies (≈ -2 eV).

The possibility of effects due to electronic polarization in the optically excited state seems common to most theoretical treatments, an example being the semicontinuum model of the F center.[31,32] The situation here is that the polarizing electrons can respond so rapidly to the slowly moving excited electron that the best stationary state must be one which includes polarization effects. An amusing if fanciful analogy with the electron-phonon problem may be made here in terms of the "electron-exciton" problem (virtual excitons are analogous to virtual phonons). If the electronic polarization could *not* "follow" the motion of the excited electron,

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[35] J. Hermanson, Phys. Rev. **150**, 660 (1966).

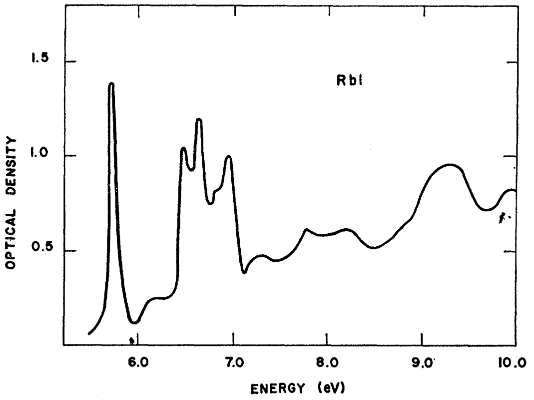

FIG. 3. Optical absorption spectrum of RbI. From 80°K data by Eby, Teegarden, and Dutton (Ref. 36).

one could have transitions into "bare" electronic states, which would then lose energy by creating excitons. One could draw configuration coordinate diagrams,[2] speak of "multi-exciton" transitions, and so forth. There would in principle also exist a "zero-exciton" transition, in which the excited electronic state would include the full electronic polarization. In fact, in real life, the "zero-exciton" transition is what is observed in normal optical absorption.

A third assumption, relevant to ionic crystals, is that holes spend most of their time on negative ions, while conduction electrons are situated on positive ions. The first of these has been widely made and is apparently rather good for the alkali halides[1,15]; the latter is probably not so good. In cases in which these corrections are being made to calculated bands, neither assumption *has* to be made; one may compute the wave-function amplitude on the two sublattices and take appropriate linear combinations of the self-energies. This has been done by the Russian workers,[19] and our results are consistent with their use of classical polarization energies in their calculations.

The method outlined in the preceding paragraph indicates how the self-energies may act to alter the shapes, as well as the positions, of energy bands. If the wave function amplitude on particular ions is a function of **k**, then so too will be the magnitude of the self-energy corrections. However, probably in most cases the rigid-shift effect will dominate changes in band shape.

There are only a few cases where comparisons can be made, at present. This is mainly because few band-structure calculations have been made; on the other hand, there exist abundant optical data for comparison. Even analysis of the optical data is not trivial, however, and we must now discuss the problem of determining the band gap from optical data.

2. *Location of the Optical Band Gap in Insulators*

In Fig. 3 we show the experimental absorption spectrum of RbI, obtained at 80°K by Eby, Teegarden, and Dutton.[36] The lowest-energy $n=1$ exciton lies at 5.8 eV; at a somewhat higher energy there lies a shoulder, followed by more structure. Similar features are observed in the other alkali halides.[36] It has been widely assumed that this shoulder, which appears in almost all of the alkali halides, represents the optical band gap. This assertion was apparently first argued convincingly by Taft and Philipp,[37] who observed external photoemission which increased rapidly for excitation energies in this region. At about the same time Fischer and Hilsch[38] examined the shoulder region in several alkali iodides and found that it actually contained one or more narrow bands. They suggested that these bands represented $n=2$ and higher exciton states, leading up to a series limit which lay ≈ 0.1 eV higher in energy than the edge of the shoulder. Baldini[39] has repeated their experiment for RbI with similar results.

That higher energy excitons leading to a series limit should exist in alkali halides is not surprising in view of their existence in the rare gases,[40] where they have been studied exhaustively. In the rare-gas case (especially xenon) the optical band gaps may be determined quite precisely in this way.

Further evidence that the series limit lies with the shoulder has come from photoconductivity studies by Nakai and Teegarden[41] and by Huggett and Teegarden.[42] The latter measurements, performed on several different alkali halides, are consistent with the series limit inferred from the exciton spectrum of RbI and show large increases in photoconductivity within the shoulder in the crystals studied.

Still more recently, Ramamurti and Teegarden[43] have measured the excitation spectra of KI and RbI, and by noting that the excitation spectra have minima at exciton peaks they can infer the positions of $n=1$, 2, and 3 exciton lines. These results, too, fit a Wannier picture, with the series limit within the shoulder.

The data just presented all favor strongly the idea that the optical band gap lies within the shoulder. The most direct theoretical evidence that this is true exists for KCl. Wood[44] pointed out that the existence of an accurate valence band calculation (that of Howland[45]) and knowledge of the electron affinity could lead to a determination of the band gap. Howland's calculation places the top of the valence band ≈ 10.7 eV below the vacuum; if one subtracts the experimental

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[36] J. E. Eby, K. J. Teegarden, and D. R. Dutton, Phys. Rev. **116**, 1099 (1960).

[37] E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids **3**, 1 (1957).

[38] F. Fischer and R. Hilsch, Nachr. Akad. Wiss. Göttingen, II Math.-Physik. Kl. **1059**, No. 8, 241 (1959); F. Fischer, Z. Physik **160**, 194 (1960).

[39] G. Baldini (unpublished, quoted in Ref. 42).

[40] G. Baldini, Phys. Rev. **128**, 1562 (1962).

[41] Y. Nakai and K. Teegarden, J. Phys. Chem. Solids **22**, 327 (1961).

[42] G. R. Huggett and K. Teegarden, Phys. Rev. **141**, 797 (1966).

[43] J. Ramamurti and K. Teegarden, Phys. Rev. **145**, 698 (1966).

[44] R. F. Wood, Solid State Commun. **4**, 39 (1965).

[45] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

electron affinity[46] (≈ 0.6 eV) from this he obtains a gap of 10.1 eV. Further subtracting the hole self-energy of 1.5 eV, we obtain an optical band gap of 8.6 eV, as compared with the photoconductivity threshold of ≈ 8.9 eV. Agreement is satisfactory.

Similar questions arise in the case of the F center, where the energy required to excite an electron directly to the conduction band has generally been assumed to be in the high-energy tail of the K band. Arguments similar to those above indicate that this picture is correct. Semicontinuum calculations, which include self-energies, place the $2p$ state before relaxation ≈ 1 eV below the conduction band[32] (in NaCl). Photoconductivity[47] increases rapidly in the high-energy tail of the K bands. A number of arguments of this sort have been made in detail by Smith and Spinolo,[48] who have shown that a semicontinuum calculation yields an interpretation of the K band as a superposition of excitations to many p states leading to a series limit in the high-energy tail.

In Table III we list exciton energies, optical bandgap energies, and their difference (the exciton binding energy) for a number of alkali and silver halides and rare gases. For RbI, KBr, KCl, and RbCl, values of E_{opt} came from Huggett and Teegarden's 80°K photoconductivity measurements.[42] Values of E_{opt} and E_{ex} for RbI and KI inferred from the 10°K data of Ramamurti and Teegarden[43] are also listed, as are those obtained at 20°K by Baldini[40] for the rare-gas solids. For the silver halides, the listed values of E_{opt} are only estimates, based upon analogies with the alkali halides. The values of E_{ex} were obtained by Okamoto[49] at 20°K. E_{ex} is obtained in most other cases from the 80°K measurements by Eby, Teegarden, and Dutton,[36] except for LiF, where we used the results of Milgram and Givens.[50] Other values of E_{opt} are estimated from the positions of shoulders in the exciton spectra, by analogy with Huggett and Teegarden's measurements which show E_{opt} to be several tenths of an eV beyond the edge of the shoulder.

TABLE III. Experimental values of the lowest $n=1$ exciton peak E_{ex}, the optical band gap E_{opt}, and their difference G_1, all in eV. Except where otherwise noted the numbers for the alkali halides are taken or inferred from the 80°K data of Eby, Teegarden, and Dutton (Ref. 36). H refers to 80°K data of Huggett and Teegarden (Ref. 42), M to room-temperature data of Milgram and Givens (Ref. 50), F to 78°K data of Fischer and Hilsch (Ref. 53), and R to 10°K data of Ramamurti and Teegarden (Ref. 43). The rare gas data at 20°K are taken from Baldini (Ref. 40), while the silver halide data at 20°K are from Okamoto (Ref. 49).

Crystal	E_{opt}	E_{ex}	G_1	Crystal	E_{opt}	E_{ex}	G_1
LiF	···	12.9^M	···	LiI	···	5.9^F	···
NaF	···	10.65	···	NaI	6.0	5.6	0.4
KF	···	9.95	···	KI	6.31^R	5.85^R	0.46
RbF	···	9.45	···	RbI	6.36^H	5.7	0.66
CsF	···	9.23	···		6.26^R	5.74^R	0.52
LiCl	8.7	8.8	−0.1	AgCl	5.5	5.1	0.4
NaCl	8.75	7.95	0.8	AgBr	4.65	4.25	0.4
KCl	8.9^H	7.8	1.1				
RbCl	8.5^H	7.5	1.0				
LiBr	7.8	7.2	0.6	Argon	14.3	12.0	2.3
NaBr	7.8	6.7	1.1	Krypton	11.67	10.17	1.50
KBr	8.0^H	6.8	1.2	Xenon	9.28	8.36	0.92
RbBr	7.8	6.6	1.2				

Several points seem worthy of comment. First, LiCl appears to have a negative exciton binding energy.[51] This fact was noted by Phillips,[52] who suggested that these transitions involved the point L in the Brillouin zone. Second, no value of E_{opt} is listed for LiI. This crystal, like LiCl, is very difficult to work with; it is hygroscopic and has a hexagonal-close-packed modification when formed from evaporation at 20°K. Fischer and Hilsch's careful studies[53] indicate that the spectrum of fcc LiI differs from those of the other iodides. The strength of the $n=1$ exciton line is quite small and it is superimposed on a continuum-like absorption, with no apparent shoulder. A similar result was noted by Taft and Philipp.[37] Finally, no numbers are listed for the optical band gaps in the fluorides; there are no photoconductivity data to guide us.

We shall discuss further aspects of the exciton problem later, and now return to consideration of the band gap.

3. *Comparison with Theory*

In KCl an accurate experimental value for the optical band gap at 80°K is 8.9 eV. Adding the self-energy correction of 3.4 eV (Table I), we see that a Hartree-Fock calculation should yield a "one-electron" gap of 12.3 eV. DeCicco[8] has used the augmented-plane-wave (APW) method to compute the KCl band structure, obtaining a one-electron gap of 6.4 eV, while the orthogonalized-plane-wave (OPW) calculation of Kahn and Quelle[9] yields ≈ 11 eV. Oyama and Miyakawa[9] have performed an OPW calculation of the conduction bands of KCl, consistent with Howland's[43] valence bands, and have obtained a band gap of 9.6 eV.

Scop[11] has performed an APW calculation of the band structure of AgCl and AgBr. He chose the crystal potentials in order to fit the optical band gaps of these materials. Since his calculation was one-electron in nature he probably should have aimed at values ≈ 5 eV higher than the direct optical gap. Scop comments that the shape of the valence bands was rather insensitive to the variations he made in his crystal potential, so the

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[46] T. Timusk and W. Martienssen, Phys. Rev. **128**, 1656 (1962).

[47] R. S. Crandall and M. Mikkor, Phys. Rev. **138**, A1247 (1965).

[48] G. Spinolo and D. Y. Smith, Phys. Rev. **140**, A2117 (1965); D. Y. Smith and G. Spinolo, *ibid.* **140**, A2121 (1965).

[49] Y. Okamoto, Nachr. Akad. Wiss. Göttingen, II Math.-Physik. Kl. IIa **14**, 275 (1956).

[50] A. Milgram and M. P. Givens, Phys. Rev. **125**, 1506 (1962).

[51] This result is somewhat uncertain. LiCl is not easy to work with and it is difficult to obtain reproducible results. [K. Teegarden (private communication).]

[52] J. C. Phillips, Phys. Rev. **136**, A1705 (1964).

[53] F. Fischer and R. Hilsch, Z. Physik **158**, 553 (1962).

results of his calculations might not change very much if he were to adjust to the larger band gaps.

According to Baldini,[40] the optical band gap in argon is 14.3 eV. Adding 2.0 eV of polarization energy, we obtain a Hartree-Fock gap of 16.3 eV. This is to be compared with 13.3 eV obtained with the APW method by Mattheiss,[5] and 12.4 eV obtained with a combined tight-binding and OPW method by Knox and Bassani.[4] For krypton, Baldini finds a gap of 11.7 eV; adding 2.3 eV, we obtain a one-electron gap of 14.0 eV. This is to be compared with the value 11.3 eV calculated by the author,[6] who used the combined tight-binding and OPW methods.

The difficulties in obtaining accurate one-electron band gaps are exemplified by noticing that the author also obtained a gap in Kr of 9.5 eV by using a slightly different exchange potential. This is an example of the existence of nontrivial corrections[1] to a given one-electron calculation which take account of the difference between model potentials (especially exchange) and Hartree-Fock potentials. These important corrections are not really within the scope of this paper, since they are one-electron in nature. It is, however, important to recognize their existence and to realize that the sorts of discrepancies mentioned above between "experimental" one-electron gaps (i.e., optical gaps minus self-energy corrections) and calculated one-electron gaps probably indicate inadequacies in the model potentials used in the calculations.

One case where model-potential corrections are probably negligible is in the aforementioned Howland calculation[45] of the KCl valence bands, for the simple reason that Howland used a Hartree-Fock approach and not a model potential. It is probably no accident that this is a case which also agrees very well with experiment, when self-energy corrections are made.

Our results may be relevant in helping to resolve some difficulties which have arisen in the determination of the optical band gap in $SrTiO_3$. The experimental gap is about 3 eV, while an ionic model which neglects polarization effects yields about 17 eV. Kahn and Leyendecker[54] attributed this discrepancy to incomplete ionicity and have obtained agreement with the experimental gap by suitably adjusting the charge on the ions. Šimánek and Šroubek[55] have criticized this analysis and have proposed that the discrepancy arises partly because of the neglect of polarization energies. Their classical calculation indicates that if the band-to-band transition involves transfer of an electron to a neighboring ion, the polarization plus electron-hole Coulomb energy is 13 eV. This removes most of the discrepancy. We point out here that they have actually "created" an exciton in transferring the electron only to a neighboring ion; in the process of creating the "free" electron-hole pair the Coulomb energy will go to zero but the polarization energy should increase considerably, perhaps enough to account for the discrepancy by itself. At any rate, the polarization energy is clearly important.

III. EFFECTS OF ELECTRONIC POLARIZATION ON BINDING ENERGIES

A. The Small-Radius Approximation for Excitations

We have shown that to compute the optical band gap one must take into account important contributions arising from electronic polarization. The next question is how polarization manifests itself in the calculation of excitation energies of small-radius states such as $n=1$ excitons. There seems to exist evidence that polarization effects are small or negligible for such states in many of the systems we are dealing with here.

This statement is probably not true for small m^* substances, particularly the silver halides, where the combination of small effective mass and large optical dielectric constant suggests that the $n=1$ exciton may be a good effective-mass state.[10]

With these exceptions in mind, we note that the damping parameters for the dielectric constants, tabulated in Table I, indicate that for most cases the dielectric effects become important only as r approaches a nearest-neighbor distance. This implies that a calculation which neglects polarization and yields a state whose radius is somewhat smaller than the nearest-neighbor distance is not likely to be changed very much when polarization is introduced.

In fact, there have been a number of successful calculations of such states in various systems in which polarization effects have been neglected. We mentioned earlier the case of the F center where Wood's Hartree-Fock calculations,[56] in which he neglects polarization have been rather successful in predicting absorption energies. Gourary and Adrian's[57] earlier point-ion calculations were also successful, and they found that including electronic polarization did not substantially affect the $1s\rightarrow 2p$ transition energies. This is also true for other centers $(M, R, \cdots)$ but it should be emphasized that this does not preclude the possibility that higher excited states of any center may accurately be described by an effective-mass approximation—in fact, there is considerable evidence that this is the case, as shown by Smith and Spinolo.[49]

Wood has extended his F-center calculations and has calculated exciton energies and wave functions for alkali halides.[58] He finds that the $n=1$ exciton has an average radius typically $\approx\frac{1}{2}$ of a nearest-neighbor distance. Earlier calculations have come to somewhat similar conclusions regarding the radius of the exciton,[59]

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[54] A. H. Kahn and A. I. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[55] E. Šimánek and Z. Šroubek, Phys. Stat. Solidi **8**, K47 (1965).

[56] R. F. Wood and H. W. Joy, Phys. Rev. **136**, A451 (1964).

[57] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[58] R. F. Wood, Phys. Rev. Letters **15**, 449 (1965).

[59] See Ref. 1 for a discussion of exciton models in the alkali halides.

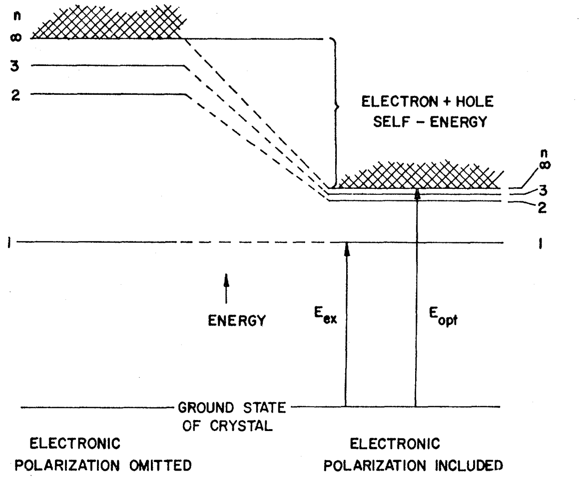

FIG. 4. Excited states of a hypothetical crystal as electronic polarization is "turned on." It is assumed that the $n=1$ exciton energy does not change, while that of all other excitons does. The quantities E_{ex} and E_{opt} are indicated, as is the sum of electron and hole self-energies.

and it seems reasonable to assume that in alkali halides the $n=1$ exciton energy is nearly independent of dielectric effects. Again, the $n=2$ and greater excitons may be well described by an effective mass theory.

In the rare gases there have been a number of calculations based upon small-radius approximations. These include older calculations performed by Knox[60] and by Gold[61] and newer ones by Sun, Rice, and Jortner,[62] by Webber, Rice, and Jortner,[63] and by Keil and Gold,[64] all of which indicate that quite satisfactory $n=1$ transition energies[40] may be obtained by completely neglecting polarization. The effective exciton radius turns out to be less than one nearest-neighbor distance, which implies that the approach is self-consistent. The transition energies in many cases are close to the free-atom values.

B. Binding Energies from Self-Energies

From the preceding sections of this paper, the following prescription for computing exciton binding energies emerges: Use the best possible Hartree-Fock theory to compute E_{ex}, neglecting polarization. Then use the same approach to obtain a one-electron band gap. Subtract from this band gap the electron and hole self-energies to obtain E_{opt}, and the binding energy is just $E_{\mathrm{opt}}-E_{\mathrm{ex}}$. For impurity states the prescription is similar.

In the absence of any such calculation, it is possible to discuss qualitatively the behavior of the binding energy. In this approach the dielectric properties of the medium are introduced not in the exciton energy *per se*; rather they enter as self-energies of the conduction electron and the valence-band hole. This statement is really in precise accord with our earlier description of the F-center problem.

The situation is illustrated in Fig. 4. Here are plotted, side by side, the optically accessible excited states *of the crystal* in two approximations, the first neglecting and the second including electronic polarization. As the polarization is "turned on" the $n=1$ excitation energy is assumed constant, while the energies of the higher states are depressed as shown. In particular, the band gap is reduced by the sum of electron and hole self-energies, and the true E_{ex} and E_{opt} are shown.

Elsewhere we describe[65] how the venerable transfer model[66] may be applied to the problem of obtaining $E_{\mathrm{opt}}-E_{\mathrm{ex}}$. This model has the virtue of describing the situation in terms of self-energies, but it is so crude that it cannot be expected to have very much quantitative validity. In the next section we shall comment further on results obtained by this model.

C. The Effective Mass Approximation

It has been common to compute exciton binding energies by means of an effective mass approximation, and in view of our rather different approach it is worth examining briefly the effective-mass results.

In the effective mass approximation[67] one obtains

$$G_n=\frac{-13.6m^*}{n^2K_0^2}\,\mathrm{eV}\,, \tag{11}$$

G_n being the binding energy of the nth state, m^* the reduced effective mass, and K_0 the optical dielectric constant. (We do not consider here states whose orbit is so large that a static dielectric constant should be used; as indicated earlier, a strict Franck-Condon approximation is made.)

In a number of cases, Eq. (11) agrees rather well with experiment for $n=1$ states, but in other cases it does not (it is generally agreed that it should work well for $n=2$ and higher states). Baldini[40] has found for both solid xenon and krypton that the $n=1$ exciton line falls within ≈ 0.2 eV of the position predicted by effective-mass theory (based upon lines of higher n). In the case of xenon in argon, however, Baldini and Knox[68] point out that the $n=1$ line is 1 eV higher in energy than predicted by effective-mass theory.

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[60] R. S. Knox, J. Phys. Chem. Solids **9**, 238, 265 (1959).

[61] A. Gold, J. Phys. Chem. Solids **18**, 218 (1961); Phys. Rev. **124**, 1740 (1961).

[62] H. Sun, S. A. Rice, and J. Jortner, J. Chem. Phys. **41**, 3779 (1964).

[63] S. Webber, S. A. Rice, and J. Jortner, J. Chem. Phys. **41**, 2911 (1964); **42**, 1907 (1965).

[64] T. H. Keil and A. Gold, Phys. Rev. **136**, A252 (1964).

[65] W. Beall Fowler, in Proceedings of the Conference on the Calculation of the Properties of Vacancies and Interstitials, Washington, D. C., 1966 (to be published).

[66] K. L. Wolf and K. F. Herzfield, *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1928), Vol. 20, Chap. 10, p. 632.

[67] W. Kohn in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

[68] G. F. Baldini and R. S. Knox, Phys. Rev. Letters **11**, 127 (1963).

In pure KI and RbI, Ramamurti and Teegarden[43] find the $n=1$ line to be within 0.1 eV of its expected position. But again, in a mixed-crystal case (I^- in RbCl) Baldini and Teegarden[69] find a discrepancy of 1 eV. In the other pure alkali halides such detailed studies have not been made, but Fischer and Hilsch[38] have shown that the binding energies of the effective-mass model [Eq. (11)] can be made to fit the observed values with reasonable values of the reduced mass.

Finally, in the semicontinuum model of the F center (Fig. 1) the computed binding energy of the $2p$ state in NaCl before lattice relaxation[32] is -1.1 eV. Using Eq. (11) with $K_0=2.31$, $m^*=0.6$, we obtain the hydrogen-atom result -0.38 eV. Here the hydrogenic result is very poor, and in fact we know that a "particle-in-a-box" model gives a much more accurate transition energy than a hydrogenic model. The unrelaxed $2p$ state simply is not very diffuse.

The question of why a small-radius state should be successfully treated by effective-mass theory has recently been studied in detail by Hermanson.[35] He has shown that the effective-mass result is susceptible to at least three corrections. These arise from the r dependence of the dielectric constant, the r dependence of the effective mass, and the repulsive pseudopotential of the core. In the case of the $n=1$ exciton in pure xenon and krypton, these corrections fortuitously cancel each other rather well (as they apparently do in the case of many pure rare gases and alkali halides).

In the case of impurities, this delicate balance is upset; there is a significant change in the repulsive core potential, but little change in $m^*(r)$ or $K(r)$. Hermanson has confirmed that the increase in core potential is sufficient to explain the anomalies associated with the binding energy of the $n=1$ state of xenon impurities in argon. No doubt a similar effect occurs for I^- in RbCl. In the case of the F center, the situation is opposite to the other two; there is no core, so the core potential is much weaker than in the exciton case and the binding energy is much larger than predicted by effective-mass theory.

That both the effective mass model and the self-energies, or transfer, model may give similar results for binding energies may be seen by the following. In the effective mass theory, G_1 varies as $1/K_0^2$. In the self-energies model[65] it varies as $[1/a](1/K_0+\text{const})$, where a is the nearest-neighbor distance. It happens that K_0 is a monotonic and sometimes linear function of a, and so if one description fits, the other may also. A similar ambiguity exists in the interpretation of thermal ionization energies of excited F centers, as we have shown.[65]

IV. SUMMARY AND CONCLUSIONS

It has been shown that the Toyozawa theory of the electronic polaron reduces to a "static" theory for the alkali halides and rare gases, and that the Haken-Schottky theory of the optical dielectric function does the same. The Mott-Littleton-type static self-energies for valence-band holes and conduction band electrons were tabulated, and we argued that these numbers represent corrections to one-electron energy-band gaps that one should make to obtain optical band gaps. This was followed by a discussion of the experimental evidence regarding the position of the optical band gap and a table of "best" values of these gaps. Several calculated energy gaps were corrected for self-energies and compared with these values.

The problem of computing the binding energies of small-radius excitations was then considered. Starting from the "localized" calculation of exciton energies, we showed that the dielectric-constant dependence of the binding energy can arise from self-energies of the "free" electron and hole. We briefly discussed the successes and failures of the effective-mass method as applied to this problem.

There are a number of areas in which further research would be helpful. On the experimental side, there are only a few alkali halides for which accurate determinations of optical band gaps and effective masses have been made. Knowledge of the ionization energies of excited impurities is likewise limited.

Theoretically, one looks for more and better band-structure calculations, possibly incorporating the polarization corrections in zeroth order. Further investigations of the applicability of the static versus dynamic approximations and possible state dependence of the self-energy corrections would also be helpful. Approaches other than the Lee-Low-Pines method should be investigated for the treatment of the electronic polaron. Application of our prescription for computing binding energies to systems other than the F center should be attempted.

ACKNOWLEDGMENTS

The author wishes to thank D. L. Dexter for his comments on a preliminary version of this paper and R. S. Knox for a number of discussions and comments. Valuable discussions were also held with D. Y. Smith, M. H. Reilly, and K. J. Teegarden. Some of this work was performed while the author was a summer visitor at Argonne National Laboratory; he wishes to thank Dr. O. C. Simpson for his kind hospitality at that time.

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[69] G. F. Baldini and K. Teegarden (unpublished).