

EXTENSION OF EFFECTIVE MASS THEORY FOR EXCITONS

MOHAMMAD A. KHATTAK

Physics Department, University of Peshawar, Peshawar

and

RALPH R. GOODMAN

US Naval Research Laboratories, Washington, D. C., USA

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Abstract. The common effective mass theory for excitons is reviewed. It is pointed out that there is a close agreement between this theory and experiments for all excitonic states except for the case $n=1$. In view of the attainable high optical resolution, this deviation is rather substantial in modern spectroscopy. We ascribe this deviation mainly to the use of static dielectric constant for all exciton radii and partly to the truncation of the effective Hamiltonian expansion at ∇^2 terms. The ordinary theory is extended here by devising a suitable interpolation formula for a non-static dielectric function and expanding the effective Hamiltonian upto ∇^4 terms. The solutions of the extended effective mass equation are obtained for $n=1$ excitons by the variational method and for higher states by the perturbation method. The results of the extended theory show remarkable agreement with experiments.

The Common Effective Mass Theory (EMT) for excitons which is briefly reviewed in the next section is known to represent, to a degree of approximation, the exciton spectra of many¹⁻³ semiconducting and insulating solids. The results of this theory agree very well with experimental findings except for the tightly bound excitons, particularly the 1S excitons. The discrepancy between theory and experiments is a general effect and is also enormous on spectroscopic standards (340 cm^{-1} in Cu_2O). In the present paper we have proposed that the discrepancy is due largely to the use of the static dielectric constant ϵ_0 for all exciton states and partly to the termination of the effective Hamiltonian expansion at ∇^2 terms. We emphasize the point that in a dielectric medium the screening of charges diminishes with decreasing distances between them. The conventional dielectric constant is actually not a constant quantity. The Bohr radius of the 1S excitons is smallest and the dielectric constant must be replaced by a dielectric function which depends on the separations between the electron and the hole. In fact, we have derived such an expression and it is of the form of an interpolation formula having the desirable feature of approaching unity for smaller separations (bare Coulomb potential) and the static constant for larger separations between the charges. We present an extension of the common EMT by incorporating a variable dielectric function into the

effect wave equation and also by expanding the effective Hamiltonian upto the ∇^4 term. We then set out to solve the proposed extended effective Schrodinger wave equation (EESWE). The initial order of magnitudes calculations shows that for states $n \geq 2$ the correction terms of the dielectric response and the ∇^4 term of the band structure can be considered as perturbations on the zero order EMT. For the state $n=1$, however, the dielectric correction term is larger than ∇^4 and is comparable with the zero order term. Therefore the solution of the EWE for the 1S exciton states was obtained by the variational method. Separate expressions have been obtained for the ∇^4 correction and the dielectric responses. The proposed theory shows that the hydrogenic $n-1$ degeneracy existing in the zero order theory is lifted and in the case of 2S and 2P states the difference should be optically resolvable. Finally, the extended EMT has been applied to the exciton spectra of Cu_2O and CuCl . Good agreement has been found between the theory and the experiments. A detailed exposition of the comparison between our calculations and the experimental observations will be reported in our next communication.

I. Review of Ordinary Effective Mass Theory (EMT).

The effective Schrodinger equation (ESE) for Wannier excitons as discussed by many authors^{4,6} is

$$\left[E_c \left(-i\nabla + \frac{\mathbf{K}}{2} \right) - E_v \left(-i\nabla + \frac{\mathbf{K}}{2} - \frac{e^2}{\epsilon\beta} \right) \right] U_{\mathbf{K}}(\beta) = E_{\mathbf{K}}(\beta) \quad \dots(1)$$

where $U_{\mathbf{K}}(\beta)$ are related to the exciton wave functions $\psi_{\mathbf{K}}$. In fact in the exciton basis functions⁶ $\psi_{\mathbf{K}\beta}$, $U_{\mathbf{K}}(\beta)$ are defined by

$$\psi_{\mathbf{K}} = \sum_{\beta} e^{-i\mathbf{K}\cdot\beta/2} U_{\mathbf{K}}(\beta) \psi_{\mathbf{K}\beta} \quad \dots(2)$$

$E_c(\mathbf{k}_e)$ is the energy of an electron in the conduction band, $-E_v(\mathbf{k}_h)$ is the energy of a hole in the valence band, β is the electron-hole separation and $\frac{e^2}{\epsilon\beta}$ represents the electron-hole potential energy diluted by the dielectric constant ϵ . $\mathbf{K} = \mathbf{k}_e - \mathbf{k}_h$ is the wave vector of an exciton formed by raising an electron from a state \mathbf{k}_h in the valence band to a state \mathbf{k}_e in the conduction band. It is known^{6,7}

that the discrete line absorption spectrum is due to $\mathbf{K}=0$ excitons. Therefore, for the sake of simplicity, but without loss of generality of the present article, we shall assume $\mathbf{K}=0$. Then Eq. (1) reduces to

$$\left[E_c(-i\nabla) - E_v(-i\nabla - \frac{e^2}{\epsilon\beta}) \right] U(\beta) = E U(\beta) \quad \dots(3)$$

Solutions of this equation will now be quickly reviewed. We call them zero order solutions.

Let ϵ in Eq. (3) be replaced by the static dielectric constant ϵ_0 . Assume that the valence and conduction bands are non-degenerate, isotropic and have extrema at $\mathbf{k}=0$. Then for \mathbf{k}_e and \mathbf{k}_h which are small compared with the size of the Brillouin zone, the band energies are given by

$$E_{c(\mathbf{k}_e)} = E_c(0) + \frac{\hbar^2 \mathbf{k}_e^2}{2m_e^*} \quad \dots(4)$$

$$E_{v(\mathbf{k}_h)} = E_v(0) - \frac{\hbar^2 \mathbf{k}_h^2}{2m_h^*} \quad \dots(5)$$

Replace \mathbf{k}_e and \mathbf{k}_h by $-i\nabla$ in (4) and (5) and substitute in (8). It gives

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{\epsilon_0\beta} \right] U(\beta) = (E - E_g) U(\beta) \quad \dots(6)$$

where $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ and $E_g(0) = E_c(0) - E_v(0)$

is the energy gap at $\mathbf{k}=0$.

This is the equation for hydrogen atom with an effective charge $\frac{e}{\sqrt{\epsilon_0}}$ from which we conclude that the bound states energies of excitons are given by

$$E_n = E_g - \frac{\mu e^4}{2\epsilon_0^2 \hbar^2 n^2} \quad \dots(7)$$

and the function $U(\beta)$ is a hydrogenic function having the form

$$U_{nlm}(\beta) = N_{nlm} R_{nl}(\beta) Y_{lm}(\theta, \phi) \quad \dots(8)$$

From Eq. (2) and (8) and the assumption that $\mathbf{k}=0$, the exciton wave functions are

$$\psi_n = \sum_{\beta} U_n(\beta) \psi_{\beta} \quad \dots(9)$$

showing that $U_n(\beta)$ is an envelope function to the zero order function of the entire electrons system. The frequency ν of the absorption lines of the crystal corresponding to the direct^{7,8} or vertical transitions is

$$h\nu = E_g - \frac{\mu e^4}{2\epsilon_0^2 \hbar^2 n^2} \quad \dots(10)$$

The above simple theory which we will call the zero order effective mass theory (EMT) for excitons represents to a degree of approximation the exciton spectrum of many crystals, e.g. Cu_2O , CuCl , CdS ,^{9,10} but an increasing discrepancy occurs with decreasing order of the quantum number n . The discrepancy is a general effect and by spectroscopic standards it is also substantial for the $n=1$ line. For example, for Cu_2O ¹ the deviation is 2.4% for the $n=1$ line but is approximately 0.5 per 10⁴ for the lines $n \geq 2$. For CuCl ⁷ the deviation is 0.7% for the $n=1$ but is less than 1 part per 10⁴ for the $n=2$ and $n=3$ lines.

We account for these deviations by making an improvement on the zero order theory. We do this by modifying the potential energy operator by a β -dependent dielectric function given by Eq. 11 as well as expanding the kinetic energy operator of the effective Hamiltonian upto the fourth power of the operator $\mathbf{k} = -i\nabla$.

II. The Extended Effective Mass Equation

A. Incorporation of the Non-static Dielectric Function. It is obvious that the screening of the interaction between two charged particles in relative motion inside a dielectric medium should depend on the frequency of their internal motion. We will regard ϵ to be a non-static dielectric constant.* We expect that when two particles are very close, the frequency of their internal motion will be so high that neither the ion-cores nor the extra-core valence electrons can follow this rapid motion. Polarization

*Strictly speaking, ϵ is no longer a constant. Dielectric function, dielectric coefficient or screening factor seems more appropriate. All of these terms will, however, be used in the sense of Eq. 11.

effects will thus be absent and the dielectric constant will then be unity. On the other hand, when the particles are far apart, the lattice of the crystal as a whole can respond to the relatively slow motion of the particles. Screening of the interaction will thus be essentially complete and ϵ will be the static dielectric constant.

A definite mathematical expression for the dielectric constant $\epsilon_{(\beta)}$, possessing the desirable feature of interpolating between the two limits $\epsilon_{(\beta)} \rightarrow 1$ as $\beta \rightarrow 0$ while $\epsilon_{(\beta)} \rightarrow \epsilon_0$ as $\beta \rightarrow \infty$ is derived in appendix A.

The result is

$$\frac{1}{\epsilon_{(\beta)}} = \frac{1}{\epsilon_0} + \frac{\epsilon_0 - 1}{\epsilon_0} \left[\frac{e^{-\kappa_e \beta} + e^{-\kappa_h \beta}}{2} \right] \dots (11)$$

where κ_e^{-1} and κ_h^{-1} are the characteristic screening distances of the crystal for the electron and the hole respectively. For $\beta > \kappa_e^{-1}$ and κ_h^{-1} the screening of the interaction between two charges is nearly complete. For $\beta < \kappa_e^{-1}$ and κ_h^{-1} the screening is breaking down and approaches rapidly towards zero for β approaching zero.

Incorporating Eq. 11 into Eq. 3, the ESE for excitons ($K=0$) in the crystalline dielectric becomes

$$\left[E_c(-i\nabla) - E_u(-i\nabla) - \frac{e^2}{\epsilon_{(\beta)}\beta} \right] U_{(\beta)} = E U_{(\beta)} \dots (12)$$

B. Expansion of EME to ∇^4 . To extend the expansion of Eq. 12 from Δ^2 upto ∇^4 terms, we will consider only crystals having cubic symmetry. The expansion of the band energies $E_n(\underline{k})$, $n=c, u$, up to k^4 terms is given in appendix B. For \underline{k} (to be replaced by $-i\nabla$) close to $\underline{k}=0$, we get the approximate expression

$$E_n(\underline{k}) = E_n(0) + \frac{\hbar^2 k^2}{2m_n^*} + C_n \left[k_x^2 + k_y^2 + k_z^2 \right] \dots (13)$$

The coefficients C_n in the above equation depends upon the crystal structure as well as the band structure of the material. It can be calculated in terms of the measurable parameters of the crystal. In particular, C_n involves the band mass m_n^* of a charge carrier and the lattice constant of the crystal. For an E.C.C crystal, C_n has been calculated in appendix B for application to cases of interest, *i.e.* Cu_2O and CuCl . Replacing \underline{k} by $-i\nabla$ in Eq. 13 and noting the defining relations for the effective masses m_e^* and m_h^* for

an electron and a hole, we have

$$E_c(-i\nabla) = E_c(0) - \frac{\hbar^2 \nabla^2}{2m_e^*} + C_c \nabla^4 \dots (14)$$

$$E_u(-i\nabla) = E_u(0) + \frac{\hbar^2 \nabla^2}{2m_h^*} + C_u \nabla^4$$

From Eq. 11, 12, 14, and 15, we finally get the extended EME for excitons as

$$-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{\beta} + C_{ev} \nabla^4 + \frac{e\Delta\epsilon}{\epsilon_0\beta} \dots (15)$$

$$\left[1 - \frac{e^{-\kappa_e \beta} + e^{-\kappa_h \beta}}{2} \right] U_{(\beta)} = (E - E_g) U_{(\beta)} \dots (16)$$

where

$$E_g = E_c(0) - E_u(0) \dots (17)$$

$$\Delta\epsilon = \epsilon_0 - 1 \dots (18)$$

$$C_{cu} = C_c - C_u \dots (19)$$

III. Solution of the Extended EME

Before we set out to solve Eq. 16 we would like to point out the following two limiting cases.

(i) $\beta \gg a$, the lattice constant, a.

In this case the ∇^4 term is much less than the ∇^2 term, and $U_{(\beta)}$ is slowly varying. Since K_e^{-1} and K_h^{-1} are of the order of few lattice constants, the exponential terms approach zero, while the remaining terms approach the value

$$-\frac{e^2}{\beta} + e^2 \frac{\Delta\epsilon}{\epsilon_0\beta} = -\frac{e^2}{\epsilon_0\beta}$$

For large β we, therefore, treat ∇^4 and the exponential terms as a perturbation on the zeroth order Hamiltonian

$$H^{(0)} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{\epsilon_0\beta} \dots (20)$$

(ii) $\beta \lesssim a$.

In this case one cannot establish as simple a criterion as for the perturbation calculations. However, it is easy to see that as β approaches zero the potential energy term approaches $-\frac{e^2}{\beta}$. This feature of the potential energy term is quite useful in selecting a suitable trial function for the variational method which we plan to use to the next section for the $n > 1$ exciton states.

A. Calculation of the $n=1$ Exciton levels by Variation Method.

Choosing the units

$$\hbar = 2\mu = \frac{e^2}{2} = 1 \dots (21)$$

the effect wave Eq. 16 in excitonic units reads as

$$\left[-\nabla^2 + C_{cv} \nabla^4 - \frac{2}{\beta} + \frac{2\Delta\epsilon}{\epsilon_0\beta} \right] \left\{ 1 - \frac{e^{-k_e\beta} + e^{-k_h\beta}}{2} \right\} (U_{\underline{\beta}}) = \epsilon U(\underline{\beta}) \quad \dots(22)$$

where

$$\epsilon = E - E_g \quad \dots(23)$$

is the binding energy of the exciton. In the present units, the units of energy and length are

$$a_{ex} = \frac{\hbar^2}{\mu e^2} = \frac{m}{\mu} a_H \quad \dots(24)$$

$$R_{ex} = \frac{\mu e^4}{2\hbar^2} = \frac{\mu}{m} R_H \quad \dots(25)$$

R_H and a_H are the conventional Rydberg and the Bohr radius.

We try the hydrogenic function for the state $n=1$ containing a variation parameter as a solution to Eq. 22. Trial solution is then

$$U_1(\alpha, \beta) = R_{10}(\alpha\beta) Y_0^0 \quad \dots(26)$$

From the table in appendix D and the normalization condition on $U_1(\alpha\beta)$ we find that

$$U_1(\alpha, \beta) = 2a^{3/2} e^{-\alpha\beta} Y_0^0 \quad \dots(27)$$

The expectation value of the Hamiltonian operator Eq. 22 in the state of the trial function Eq. 27 is

$$\epsilon_1(\infty) = \langle U_1 | -\nabla^2 - \frac{2}{\beta} + C_{cv} \nabla^2 + \frac{2\Delta\epsilon}{\epsilon_0} \left[1 - \frac{e^{-\kappa_e\beta} + e^{-\kappa_h\beta}}{2} \right] U_1 \rangle \quad \dots(28)$$

It is straightforward to evaluate the right hand side of Eq. 28. We obtain

$$\epsilon_1(\alpha) = \alpha^2 - 2\alpha + 5C_{cv}\alpha^4 + \frac{2\Delta\epsilon}{\epsilon_0} \left[\alpha - \frac{2\alpha^3}{(\alpha - \kappa_e)^2} - \frac{2\alpha^3}{(2\alpha + \kappa_h)^3} \right] \quad \dots(29)$$

Minimizing $\epsilon_1(\alpha)$ with respect to the parameter α requires

$$\begin{aligned} \frac{\partial \epsilon_1}{\partial \alpha} &= \epsilon_1'(\alpha) \\ &= 2\alpha - 2 + 20 C_{cv} \alpha^3 \\ &+ \frac{2\Delta\epsilon}{\epsilon_0} \left[1 - \frac{\alpha^2}{(2\alpha + \kappa_e)^2} - \frac{\alpha^2}{(2\alpha + \kappa_h)^2} \right] \\ &+ \frac{2\Delta\epsilon}{\epsilon_0} \left[\frac{8\alpha^3}{(2\alpha + \kappa_e)^3} + \frac{8\alpha^3}{(2\alpha + \kappa_h)^3} \right] = 0 \quad \dots(30) \end{aligned}$$

This is a sixth degree equation in α . Finding its roots α_0 in terms of the given parameters of the

crystal C_{cv} , ϵ_0 , κ_e and κ_h , the energy of the $n=1$ exciton state in a particular crystal can be calculated. The energy of the state after some simplification of Eq. 29 is obtained to be

$$\epsilon_1 = a_0^2 - \frac{2a_0}{\epsilon_0} + 5 C_{cv} a_0^4 - \frac{\epsilon_0 - 1}{\epsilon_0} \left[\frac{1}{\left(1 + \frac{\kappa_e}{2a_0}\right)^2} + \frac{1}{\left(1 + \frac{\kappa_h}{2a_0}\right)^2} \right] \quad \dots(31)$$

B. Solution of the Wave Equation for $n \geq 2$ States The Perturbation Approach

In this case we write Eq. 22 in the alternative form

$$\left[-\nabla^2 - \frac{2}{\epsilon_0\beta} + C_{cv} \nabla^4 - \frac{\epsilon_0 - 1}{\epsilon_0} (e^{-\kappa_e\beta} + e^{-\kappa_h\beta}) \right] U(\underline{\beta}) = \epsilon U(\underline{\beta}) \quad \dots(32)$$

For $n \geq 2$, the exciton orbits in dielectric crystals are approximately equal to or greater than $20a$, where a is the lattice constant. It was pointed out earlier that for such cases the last two terms can be considered as a perturbation as the first two terms. The solutions of the zeroth order Eq. 6 are then given by Eq. 8.

To the first order of the perturbation the exciton energies for the states $n \geq 2$ are

$$\begin{aligned} \epsilon_{nl} &= -\frac{1}{\epsilon_0 n^2} + C_{cv} \langle U_{nlm}^0 | \nabla^4 | U_{nlm}^0 \rangle \\ &- \frac{\Delta\epsilon}{\epsilon_0} \langle U_{nlm}^0 | \frac{e^{-\kappa_e\beta} + e^{-\kappa_h\beta}}{\beta} | U_{nl}^0 \rangle \quad \dots(33) \end{aligned}$$

Evaluating the integrals* contained in the above equation we obtain that for $n \geq 2$

$$\epsilon_{nl} = -\frac{1}{\epsilon_0 n^2} - \frac{4C_{cv}}{\epsilon_0 n^3} \left[\frac{3}{4n} - \frac{1}{1 + \frac{1}{2}} - \sum_{nl}^{(d)} (\kappa_e, \kappa_h) \right] \quad \dots(34)$$

The last two terms in Eq. 34 are respectively the k^4 and the dielectric corrections to the zero order hydrogenic energies.

A general expression for the dielectric correction terms given by

$$\epsilon_{nl}^{(d)}(\kappa_e, \kappa_h) = \frac{\epsilon_0 - 1}{\epsilon_0} \langle R_{nl} | \frac{e^{-\kappa_e\beta} + e^{-\kappa_h\beta}}{\beta} | R_{nl} \rangle \quad \dots(35)$$

*For the evaluation of some of the integrals and the behaviour of the hydrogen functions Pauling and Wilson¹¹ as well as Condon and Shortley¹² are recommended.

is not attempted. However for those values of n and l which really matter in Wannier excitons Eq. 35 is evaluated. For evaluations of the integrals in Eq. 35, the hydrogenic functions $R_{nl}(\beta)$ have to be modified by the dielectric constant ϵ_0 . A list of these modified functions (prepared from Pauling and Wilson¹¹) is given in appendix C. The results of calculations for $\mathcal{E}_{nl}^d(k_e, k_h)$ is given below:

$$\mathcal{E}_{20}^d = \frac{\epsilon_0 - 1}{4\epsilon_0^2}$$

$$\mathcal{E}_{i=e,h} \left[\frac{2}{[1 + \epsilon_0 k_i]^2} - \frac{4}{[1 + \epsilon_0 k_i]^3} + \frac{3}{[1 + \epsilon_0 k_i]^4} \right] \dots (36a)$$

$$\mathcal{E}_{21}^d = \frac{\epsilon_0 - 1}{4\epsilon_0^2} \sum_{i=e,h} \frac{1}{[1 + \epsilon_0 k_i]^4} \dots (36b)$$

$$\mathcal{E}_{30}^d = \frac{\epsilon_0 - 1}{9\epsilon_0^3} \frac{4}{2187} \sum_{i=e,h} \left[\frac{729}{[\frac{2}{3} + \epsilon_0 k_i]^2} - \frac{1944}{[\frac{2}{3} + \epsilon_0 k_i]^3} + \frac{1944}{[\frac{2}{3} + \epsilon_0 k_i]^4} - \frac{1728}{[\frac{2}{3} + \epsilon_0 k_i]^5} + \frac{480}{[\frac{2}{3} + \epsilon_0 k_i]^6} \right] \dots (36c)$$

$$\mathcal{E}_{31}^d = \frac{\epsilon_0 - 1}{9\epsilon_0^3} \frac{8}{2187}$$

$$\mathcal{E}_i \left[\frac{216}{[\frac{2}{3} + \epsilon_0 k_i]^4} - \frac{288}{[\frac{2}{3} + \epsilon_0 k_i]^5} + \frac{120}{[\frac{2}{3} + k_e]^6} \right] \dots (36d)$$

$$\mathcal{E}_{32}^d = \frac{\epsilon_0 - 1}{9\epsilon_0^3} \frac{8}{2187} \sum_i \frac{24}{[\frac{2}{3} + \epsilon_0 k_i]^6} \dots (36e)$$

Eq. 31 and 36 are general equations for the energy levels of Wannier excitons. For a particular crystal, its parameters m_e^* , m_h^* , C_{cv} , k_e , k_h , if known are to be inserted in the above equations. We apply them to the exciton spectra of Cu_2O and CuCl . The results of our calculations and comparison with experimental data will be reported in our next communication.

IV. Discussion

In order to apply the extended effective mass theory, developed in the preceding sections, to any specific case, we need to know the various parameters m_e^* , m_h^* , C_c , C_v , ϵ_0 , k_e and k_h . At present, however, all of them are not known to us from experiments. One needs to calculate C_c , C_v , k_e and k_h from theoretical considerations. These calculations have been carried by the authors and will be reported in our next communication. The screening parameters k_e and k_h were calculated from the exciton spectra

of the crystal under consideration whereas C_c and C_v were computed from the band structure and crystal structure of the material. Comparison of theoretical results with experimental findings suggests the success of our proposed theory. The theory shows that the $n=2$ state splits in principle into two optically resolvable states whereas the $n=1$ degeneracy of higher states is lifted but not to a resolvable extent.

It may be noted that solutions of the EEME (Eq. 16) were obtained by the variational method for IS excitons and by the perturbation method for the higher states. It seems possible and more desirable to attempt a single unified method of solving the EEME which will be valid for all excitonic states and give the solutions in a closed form of known functions.

Appendix A. Space dependent interpolation of the dielectric constant of a semiconductor. In this appendix we wish to show the validity of the interpolation formula for the dielectric coefficient $\epsilon(\beta)$. Since the Fourier transform of the unscreened

Coulomb potential $\frac{1}{r}$ is $\frac{4\pi}{q^2}$, therefore, the screened potential is given approximately by

$$V_s(r) = 4\pi \int_{\text{entire space}} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q^2 \epsilon(\mathbf{q}, g=0)} d\mathbf{q} \dots (A-1)$$

where \mathbf{g} is a reciprocal lattice vector.

For semiconductors at low temperatures (strictly $T=0^\circ\text{K}$) the screening factor

$$\epsilon(\mathbf{q}, 0) = 1 + \frac{4\pi e^2}{q^2} \sum_{\mathbf{c}, \mathbf{k}} \frac{\langle C_{\mathbf{k}+\mathbf{q}} | e^{i\mathbf{q}\cdot\mathbf{r}} | U_{\mathbf{k}} \rangle}{E_c(\mathbf{k}+\mathbf{q}) - E_v(\mathbf{k})} \dots (A-2)$$

Let us note at this stage that as $\mathbf{q} \rightarrow 0$, $\epsilon(\mathbf{q}, 0) \rightarrow \epsilon_0$

whereas when \mathbf{q} tends towards the zone boundary,

$\epsilon(\mathbf{q}, 0) \rightarrow 1$. Therefore, the expression for $V_s(\mathbf{r})$ has

the correct asymptotic behaviour in that it approaches $\frac{1}{\epsilon_0 r}$ as r approaches infinity. In order to include the screening effects for all values of r we follow Hermanson and Phillips¹³ and define the r -dependent dielectric coefficient by the equation

$$V_s(r) = \frac{1}{\epsilon(r)r} \dots (A-3)$$

Comparing Eq. A-3 and A-1, we get

$$\frac{1}{\epsilon(r)} = 4\pi r \int_{\text{entire space}} \frac{e^{i\mathbf{q}\cdot\mathbf{r}}}{q^2 \epsilon(\mathbf{q}, 0)} d\mathbf{q} \dots (A-4)$$

The next step is to calculate $\epsilon(\underline{q}, 0)$. Since $\epsilon_0 = \epsilon(\underline{q}=0, 0)$ we obtain from Eq. A-2

$$\epsilon(\underline{q}, 0) = 1 + (\epsilon_0 - 1) \frac{f(\underline{q})}{f(0)} \dots (A-5)$$

where $f(\underline{q})$ is the second term on the right hand side of Eq. A-2. For a large energy gap and hole mass very large compared with the electron mass Herman-son has developed a Lorentzian expression for $f(\underline{q})$ and consequently calculates $\epsilon(\underline{r})$ to be given by

$$\frac{1}{\epsilon(\underline{r})} = \frac{1}{\epsilon_0} + \frac{(\epsilon_0 - 1)}{\epsilon_0} e^{-\kappa_h r} \dots (A-6)$$

where the dielectric breakdown length κ^{-1} is treated as a parameter. For hole mass comparable with the electron mass and energy gaps of the order of capital photon energies we replace Eq. A-6 by

$$\frac{1}{\epsilon(\underline{r})} = \frac{1}{\epsilon_0} + \frac{\epsilon_0 - 1}{\epsilon_0} \left[\frac{e^{-\kappa_e r} + e^{-\kappa_h r}}{2} \right] \dots (A-7)$$

Letting r equal to β we get Eq. 14.

If an analogy is drawn between Eq. 7 and Haken's¹⁴ interpolation formula in which phonon-electron interactions are responsible for the modification of the static dielectric constant then κ_e and κ_h are related to a characteristic frequency of the crystal, ω , and the effective masses of the electron and hole by

$$\kappa_i = \left(\frac{2m_i^* \omega}{h} \right); i = e, h \dots (A-8)$$

Appendix B. Expansion of $E_n(\underline{k})$ and calculation of C_{nm} .

Band states satisfy the equation

$$\mathcal{H} \psi_{n\underline{k}} = E_{n\underline{k}} \psi_{n\underline{k}} \dots (B-1)$$

Let

$$\psi_{n\underline{k}} = N^{-\frac{1}{2}} \sum_{\underline{R}} e^{-i\underline{k} \cdot \underline{R}} a_n(\underline{r} - \underline{R}) \underline{dr} \dots (B-2)$$

then

$$E_{n(\underline{k})} = \sum_{\underline{R}} \epsilon_{n\underline{R}} e^{i\underline{k} \cdot \underline{R}} \dots (B-3)$$

where

$$\sum_{n\underline{R}} = \int a_n(\underline{r}) \mathcal{H} a_n(\underline{r} - \underline{R}) \underline{dr} \dots (B-4)$$

and $a_n(\underline{r})$ are Wannier⁴ functions.

We consider an F. C. C. crystal (Cu_2O) and approximate Eq. B-3 by extending the summation only to nearest neighbours. For an F. C. C. crystal the nearest neighbours are at

$$\underline{R}_{\text{NN}} = (\pm 1, \pm 1) \frac{d}{2}, (\pm 1, 0, \pm 1) \frac{d}{2}$$

$$\text{and } (0, \pm 1, \pm 1) \frac{d}{2} \dots (B-5)$$

where d is the edge length of the cube. Assuming an s -character and negligible overlap of the Wannier functions, $\sum_{n\underline{R}_{\text{NN}}}$ will be the same for all $\underline{R}_{\text{NN}}$. To

fourth order of \underline{k} we therefore obtain from Eq. B-3

$$E_{n(\underline{k})} = \epsilon_n^{(0)} + \epsilon_{n,1,1,0} d^2 \left[-K^2 + \frac{d^2}{48} (k_x^2 + k_y^2 + k_z^2 + \dots + 3k_x^2 k_z^2) \right] \dots (B-8)$$

For a conduction band having energy minimum at $\underline{k}=0$, we let

$$-\epsilon_{c,1,1,0} d^2 = \frac{\hbar^2}{2m_e^*} \dots (B-7)$$

and similarly for the valence band having a maximum at $\underline{k}=0$ we let

$$-\epsilon_{v,1,1,0} d^2 = \frac{\hbar^2}{2m_h^*} \dots (B-8)$$

Hence making this substitution,

$$E_{c(\underline{k})} = \epsilon_c(0) + \frac{\hbar^2 k^2}{2m_e^*} = \frac{\hbar^2 d^2}{96m_e^*} \left[k_x^4 + k_y^4 + \dots + 3k_x^2 k_z^2 \right] \dots (B-9)$$

$$E_{v(\underline{k})} = \epsilon_v(0) - \frac{\hbar^2 k^2}{2m_h^*} + \frac{\hbar^2 d^2}{96m_h^*} \left[k_x^4 + k_y^4 + \dots + 3k_x^2 k_z^2 \right] \dots (B-10)$$

Now making spherical approximation, *i.e.* replacing $2(k_x^2 k_y^2 + k_y^2 k_z^2 + k_z^2 k_x^2)$ by $3/5 k^4$, etc., we obtain

$$E_c(\underline{k}) = \epsilon_c(0) + \frac{\hbar^2 k^2}{2m_e^*} - \frac{\hbar^2 d^2}{80m_e^*} k^4 \dots (B-11)$$

$$E_v(\underline{k}) = \epsilon_v(0) - \frac{\hbar^2 k^2}{2m_h^*} + \frac{\hbar^2 d^2}{80m_h^*} k^4 \dots (B-12)$$

Hence the coefficients of the k^4 terms are

$$C_c = -\frac{\hbar^2 d^2}{80m_e^*} \dots (B-13)$$

$$C_v = \frac{\hbar^2 d^2}{80m_h^*} \dots (B-14)$$

and

$$C_{cv} = C_c - C_v = -\frac{\hbar^2 d^2}{80 \mu} \quad \dots(B-15)$$

where μ is the reduced electron-hole mass.

In excitonic units $\hbar = 2\mu = \frac{e^2}{2} = 1$

$$C_{cv} = -\frac{d^2}{40 a_{ex}^2} \quad \dots(B-16)$$

Appendix C. The Hydrogenic Radial Wave Functions $R_{nlm}(r/\epsilon_0)$. In a system of units $\hbar = 2\mu = e^2/2 = 1$ and an interaction potential energy $-e^2/\epsilon_0 r$ the radial functions are listed below:

$$R_{10} = \epsilon_0^{-3/2} 2 e^{-r/\epsilon_0}$$

$$R_{20} = \frac{\epsilon_0^{-3/2}}{\sqrt{8}} (2 - r/\epsilon_0) e^{-r/2 \epsilon_0}$$

$$R_{21} = \frac{\epsilon_0^{-3/2}}{\sqrt{24}} r/\epsilon_0 e^{-r/2 \epsilon_0}$$

$$R_{30} = \frac{2 \epsilon_0^{-3/2}}{81 \sqrt{3}} (27 - 18r/\epsilon_0 + 2(r/\epsilon_0)^2) e^{-r/3 \epsilon_0}$$

$$R_{31} = \frac{4 \epsilon_0^{-3/2}}{81 \sqrt{6}} r/\epsilon_0 (6 - r/\epsilon_0) e^{-r/3 \epsilon_0}$$

$$R_{32} = \frac{4 \epsilon_0^{-3/2}}{81 \sqrt{30}} r^2/\epsilon_0^2 e^{-r/3 \epsilon_0}$$

For the continuation of this list Pauling and Wilson or Condon and Shortley are recommended.

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