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Relationes

Exact Solution of an Electron Trapped in a Spherical Cavity and Applications to the *F* Center in Alkali Halides*

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An exact solution of the Schrödinger equation for an electron trapped in a spherical cavity of the Krumhansl and Schwartz potential is given. Transition energies ($1S \rightarrow 2P$) of the F electron are reported for 16 MX systems and the normalization constants of the wave functions are given for the $1S$ and $2P$ states. The shape of absorption bands of F-centers is also discussed and the calculated oscillator strengths for the transition $1S \rightarrow 2P$ of various crystals are given.

Introduction

The problem of an electron trapped at a spherical cavity in an otherwise continuous dielectric media has received attention for nearly three decades. The problem is of interest because it has been used as a model of the F center in alkali halides. A numerical treatment was given by Tibbs [1]. This was followed by a variation treatment given by Simpson [2] and a perturbation calculation given by Krumhansl and Schwartz [3]. These three calculations also utilized three slightly different potentials although qualitatively they are all equivalent; the potential energy is taken as constant within the sphere and varies as $1/k_o r$ outside the sphere. Arguments for this form of potential have been given [1–4].

Calculations

The potential energy as given by Krumhansl and Schwartz [3] is composed of three terms. Firstly, there is the Madelung energy, $-\alpha_M/R$, where α_M is the Madelung constant and R is the nearest neighbor distance. Strictly speaking this is the only place where account is made of the lattice structure. Secondly, there is the repulsive polarization energy, $\frac{1}{2R}\left(1-\frac{1}{k_o}\right)$ where k_o is the static dielectric constant. The static dielectric constant is used because the ions are assumed to be fixed at their lattice sites. Also, the use of k_o instead of optical k_∞ is suggested by the fact that during any optical transition the ions will not have time to relax [5]. Thirdly, there is an adjustment of the potential energy to refer it to the bottom of the conduction band (instead of the vacuum) and this amounts to subtracting x, the electron affinity of the crystal.

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The potential energy is thus

$$V_i = -\frac{\alpha_M}{R} + \frac{1}{2R}\left(1 - \frac{1}{k_o}\right) - x \qquad \text{(inside the cavity)} \tag{1}$$

and

$$V_o = -1/k_o r\,. \qquad \text{(outside the cavity)} \tag{2}$$

In both of these regions the Schrödinger equation is separable and yields the spherical harmonics as solutions to the angular portion of the problem. We are left with Eqs. (3) and (4) for the radial part of the problem inside and outside of the sphere respectively as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_i}{dr}\right) + \left[-2V_i + 2E - \frac{l(l+1)}{r^2}\right]R_i = 0 \tag{3}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_o}{dr}\right) + \left[2E + \frac{2}{k_o r} - \frac{l(l+1)}{r^2}\right]R_o = 0\,. \tag{4}$$

The solution of (3) satisfying the appropriate quantum mechanical boundary condition is [6]

$$R_i(r) = A j_l(\alpha r) \tag{5}$$

with $\alpha^2 = 2E - 2V$. $j_l(\alpha r)$ are the spherical Bessel functions.

Equation (4) can be transformed into Whittaker's equation

$$W\left(\frac{1}{\beta k_o}, l + \frac{1}{2}, z\right)'' + \left[-\frac{1}{4} + \frac{1}{\beta k_o z} - \frac{l(l+1)}{z^2}\right] W\left(\frac{1}{\beta k_o}, l + \frac{1}{2}, z\right) = 0\,, \tag{6}$$

the satisfactory solution of which is [7]

$$W(k, m, z) = \frac{e^{-z/2} z^k}{\Gamma\left(\frac{1}{2} - k + m\right)} \int_0^\infty t^{-k-\frac{1}{2}+m}\left(1 + \frac{t}{z}\right)^{k-\frac{1}{2}+m} e^{-t}\,dt \tag{7}$$

for $k - \frac{1}{2} - m < 0$.

The spherical Bessel functions are to be matched to the Whittaker functions at the boundary. Making use of recursion relations [7], we find

$$\alpha\frac{j_{l-1}(\alpha R)}{j_l(\alpha R)} - \frac{l}{R} = \beta - \frac{W\left(\frac{1}{\beta k_o} + 1, l + \frac{1}{2}, 2\beta R\right)}{R \cdot W\left(\frac{1}{\beta k_o}, l + \frac{1}{2}, 2\beta R\right)}\,. \tag{8}$$

To evaluate the ratio of the W's in Eq. (8) we can make use either of Eq. (7) or of asymptotic series given by Whittaker and Watson [7]

$$W(k,m,z) = e^{-\frac{1}{2}z} z^k \left\{1 + \frac{m^2 - \left(k - \frac{1}{2}\right)^2}{1!\,z} + \frac{\left[m^2 - \left(k - \frac{1}{2}\right)\right]\left[m^2 - \left(k - \frac{3}{2}\right)^2\right]}{2!\,z^2} + \cdots\right\}. \tag{9}$$

Using Eqs. (8) and (7) or (9) and writing α as $\alpha = \sqrt{-2V_i - \beta^2}$ gives an equation in β which can be solved to any desired degree of accuracy by numerical methods. Thus we can determine the eigenvalues from Eq. (8) and the eigenfunctions from Eq. (5) and Eq. (7), or Eq. (9).

Application to *F* Centers

Table 1 gives the various quantities of *F* centers to be used for the calculation of the energy. In the calculation of energy of *F* centers we have used the crystal electron affinity as given by Tibbs for NaCl as 0.5 eV for all the crystals

Table 1. *Parameters used and calculated in the energy computations and energies and spectra for the $K-S$ potential*

Crystal	R(a.u.)	k_0	V_0(a.u.)	E_{1S}	E_{2P}	ΔE(calc) ($1S\rightarrow 2P$)	ΔE(exp) ($1S\rightarrow 2P$)
LiH	3.859	3.61	0.3775	5.430	1.309	4.12	2.4
LiF	3.794	1.92	0.4152	6.456	2.296	4.16	4.96
LiCl	4.84	2.75	0.3137	5.264	2.231	3.03	3.22
LiI	5.67	3.80	0.2616	4.609	2.176	2.43	2.33
NaF	4.37	1.74	0.3696	6.241	2.810	3.43	3.65
NaCl	5.317	2.25	0.2947	5.245	2.633	2.62	2.67
NaBr	5.63	2.62	0.2739	4.930	2.497	2.26	2.30
NaI	6.11	2.91	0.2507	4.625	2.497	2.13	2.11
KF	5.03	1.85	0.3202	5.691	2.892	2.80	2.72
KCl	5.94	2.13	0.2684	5.001	2.816	2.19	2.20
KBr	6.24	2.33	0.2527	4.766	2.704	2.07	1.97
KI	6.65	2.69	0.2340	4.475	2.623	1.82	1.81
RbF	5.33	1.93	0.3016	5.449	2.865	2.58	2.60
RbCl	6.18	2.19	0.2572	4.864	2.799	2.07	1.98
RbBr	6.47	2.33	0.2444	4.677	2.748	1.93	1.72
RbI	6.92	2.63	0.2261	4.388	2.655	1.73	1.60

investigated, and we have used the interatomic distance as the radius of the cavity instead of the more sophisticated radii advocated by Mott and Littleton [8]. Fig. 1 shows an Ivey plot for the $1S\rightarrow 2P$ transition and this is compared with the experimental data on F centers. Table 1 gives the energies of E_{1S} and E_{2P} of F centers for various crystals and the experimental values of $\Delta E_{1S\rightarrow 2P}$ for comparison.

In Table 2 we present the values of the oscillator strength for the $1S\rightarrow 2P$ transition. The definition of oscillator strengths is given by

$$f=\frac{8\pi^2}{3h}\,vm|\langle b|r|a\rangle|^2\,. \tag{10}$$

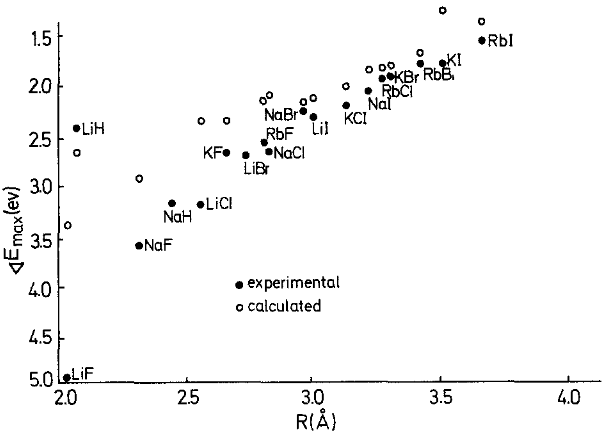

Fig. 1. Ivey plot of experiment and calculated data

These calculated f values are very close to those calculated by Gourary and Adrian [9] for the point ion lattice. The solution as given above is also of use in a similar problem developed by Gourary and Adrian [9]. They treat the crystals as a system of point ions with an electron in place of one anion. The general feature of the Whittaker functions to be used as the resulting wavefunctions from the APW method seems to be promising. Work in this area is currently in progress.

The potential energy functions studied in this paper describe the primary electronic transition ($1S \rightarrow 2P$) to a high degree of accuracy. A brief but further study of transitions to higher electronic states, i.e. the $3P$ or $3D$ levels, indicates that at best the calculated transition energies are only in qualitative agreement with the observed transitions apparent in the K and L bands of colored crystals.

Table 2. *Oscillator strengths of the $1S \rightarrow 2P$ transition of the F center*

Crystal	$f_{1S \rightarrow 2P}$(this work)	f (Calc. by others)	f (exp.)
NaCl	0.995	0.61[a], 0.97[b]	0.7[c]
NaBr	0.92		
KCl	0.98	0.99[b]	0.66[c], 0.85[d]
KI	0.97		1.17[e]
			0.46[c]
RbF	0.98		

[a] S. Tibbs [1].

[b] B. Gourary and F. Adrian [9].

[c] C. Rauch and C. Heer: Physic. Rev. **105**, 914 (1957).

[d] R. Silsbee [15].

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The calculated energy differences were $\Delta E_{1S \rightarrow 3P} \simeq 4.5$ eV and $\Delta E_{1S \rightarrow 3D} \simeq 4.5$ eV for KCl. For KCl the peak energies are as follows $\Delta E_K = 2.71$ eV, $\Delta E_{L_1} = 3.60$ eV, $\Delta E_{L_2} = 4.30$ eV, and $\Delta E_{L_3} = 4.94$ eV.

Next we apply the above calculation of the shape of absorption bands of F centers. Many attempts [10–14] have been made to explain the shape of absorption bands of F centers in solid systems. If, for simplicity, one assumes that all lattice modes have the same frequency ω, then the absorption coefficient can be expressed as:

$$\alpha_{a \rightarrow b}(\nu) = \frac{16\pi^4 \nu}{3hnc\omega} |\langle a|er|b\rangle|^2 \exp\left\{[-S(2\bar{n}+1)] \left(\frac{\bar{n}+1}{\bar{n}}\right)^{\frac{1}{2}P} I_P[2S\sqrt{\bar{n}(1+\bar{n})}\right\} \quad (11)$$

where n is the refractive index, c is the speed of light, $\bar{n} = [\exp(h\omega/kT) - 1]^{-1}$ S is the Huang-Rhys S-factor [10]. $P = \frac{2\pi}{\omega}(\nu - \nu_{ab}) + B(2\bar{n}+1)$ and $I_p(x)$ is the Bessel functions of imaginary argument [7]. B is defined as $B = \frac{1}{2} N\varrho$, where ϱ is the modification of lattice frequencies between the two electronic states. Applying Eq. (11) to Silsbee's data for the KCl crystal [15], we determine S and B as $S = 13.0$

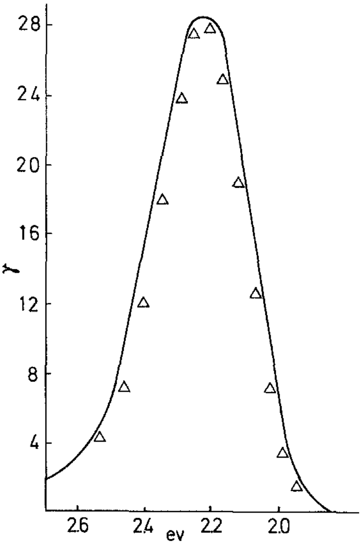

Fig. 2. Spectrum of the *F*-band in KCl at 300° K. The solid line is the data of Silsbee. The triangles indicate the calculated spectrum

and $B = 5.0$ from the optical density and corresponding wavelength at the maximum and at one other point. Then putting S, B and our calculated value of $|\langle a|er|b\rangle|^2$ in Eq. (11), we can determine the absorption coefficient as a function of frequencies. The results are shown in Fig. 2 by open triangles. While the agreement is not perfect, the error for the most part is less than 10%.

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