F-center optical absorption in alkali halides

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Abstract. The transition energies of F-centers for six alkali halides are calculated with the point-ion approximation and the ion-size correction. We show the correct expression of the energy functional for the Gourary and Adrian wave function of type II. We compare our results with other works and find that they do not differ by more than 13% from the experimental results, except for LiI, with $\alpha = 0.53$.

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1. Introduction

Recently we have studied the optical absorption of F and F_A-centers in CsF [1] and in KCl:KBr [2], as well as the optical absorption of F-centers in mixed crystals [3]. In those studies, we have calculated the transition energies using the Bartram, Stoneham and Gash method [4] and Gourary and Adrian [5] trial wave functions.

It is interesting to notice that Alig [6] developed a similar methodology but he considered the Phillips and Kleinman [7] form of the repulsive potential.

It is also known that Weber and Dick [8] found an error in the expression of Gourary and Adrian energy functional [5] for the ground state function of type II. Nevertheless, they never showed the correct expression.

That wrong expression was used to calculate the optical absorption energies of F and F_A-centers in cesium halides [9,10], and therefore Ruiz-Mejía [11] showed that the results given in those papers were probably incorrect.

In this work we show the correct energy functional expression and compare our results with other works.

2. Theory

In the Bartram *et al.* method [4] the ground and first excited state energies are obtained by minimizing the energy functional

$$E_{\rm IS}(\xi) = E_{\rm PI} + \sum_{\gamma}\Big(A_\gamma + (\bar{V}_{\rm P} - U_\gamma)B_\gamma\Big)|\Phi(r_\gamma)|^2, \qquad (1)$$

where ξ is the parameter which is varied to minimize Eq. (1) with $\bar{V}_{\rm P}$ fixed. $E_{\rm PI}$ is

the point-ion approximation. The last term represents the ion-size correction

$$V_{\mathrm{P}} = \sum_{\gamma} \Big(A_{\gamma} + (\bar{V}_{\mathrm{P}} - U_{\gamma}) B_{\gamma} \Big) \delta(r - r_{\gamma}), \tag{2}$$

where

$$\bar{V}_{\mathrm{P}} = \bar{V}_{\mathrm{PI}} + \bar{V}_{\mathrm{IS}}. \tag{3}$$

Here $\bar{V}_{\mathrm{PI}}$ and $\bar{V}_{\mathrm{IS}}$ are the expectation values of the point-ion potential and ion-size correction respectively, U_{γ} is the potential at the γ-th ion due to all the other ions, and A_{γ} and B_{γ} are characteristic parameters of the ions.

To obtain the point-ion approximation E_{PI}, it is considered that the electron which forms the F-center has a potential energy of the form

$$V_{\mathrm{PI}}(r) = \sum_{x_i, y_i, z_i = -\infty}^{\infty}{}' (-1)^{x_i + y_i + z_i} \Big((x - a x_i)^2 + (y - a y_i)^2 + (z - a z_i)^2 \Big)^{-1/2}. \tag{4}$$

In Eq. (4), a is the nearest neighbor distance, $(a x_i, a y_i, a z_i)$ are the coordinates of the i-th ion, and the prime on the summation sign means that the point $(0, 0, 0)$ is omitted. Then

$$E_{\mathrm{PI}} = \frac{\int \left\{ \Phi^{*}(r) \left[-\frac{1}{2} \nabla^2 + V_{\mathrm{PI}}(r) \right] \Phi(r) \right\} d\tau}{\int |\Phi(r)|^2 d\tau}, \tag{5}$$

where $\Phi(r)$ is a trial wave function. The Gourary and Adrian wave function of type II for the ground state is

$$\Phi(r) = \begin{cases} A j_0 \left(\dfrac{\xi r}{a} \right) \exp(-\eta), & r < a \\ A j_0(\xi) \exp \left(\dfrac{-\eta r}{a} \right), & r > a \end{cases} \tag{6}$$

where

$$\eta = 1 - \xi \cot \xi, \tag{7}$$

and for the first excited state is

$$\Phi(r) = \begin{cases} A' j_1\left(\frac{\xi' r}{a}\right) \exp(-\eta'), & r < a \\ A' j_1(\xi')\left(\frac{r}{a}\right) \exp\left(-\frac{\eta' r}{a}\right), & r > a \end{cases} \tag{8}$$

where

$$\eta' = 3 - \xi'^2 (1 - \xi' \cot \xi')^{-1}. \tag{9}$$

Here A and A' are the normalizing constants and ξ and ξ' are the variational parameters respectively.

Using Eq. (5) we obtain for the ground state

$$E_{\mathrm{PI}}^{b} = \frac{1}{2a^2}\left\{\xi^2 - \frac{G(\xi)}{\eta}\left[\eta^2 - \eta - \frac{1}{2} + \xi^2\left(1 + \frac{1}{\eta} + \frac{1}{2}\eta^{-2}\right)\right]\right\}$$

$$- \frac{1}{a}\left\{\alpha_M - \frac{1}{2}\eta^{-3} G(\xi) \sum_{z_i \geq y_i \geq x_i \geq 0}{}' h_i (-1)^{x_i + y_i + z_i} \frac{(1 + \rho_i \xi)}{\rho_i} \exp[-2\eta(\rho_i - 1)]\right\} \tag{10}$$

where

$$[G(\xi)]^{-1} = \left[1 - \frac{1}{2\xi} \operatorname{sen} 2\xi\right] (\operatorname{sen} \xi)^{-2} + \frac{1}{\eta}\left(1 + \frac{1}{\eta} + \frac{1}{2}\eta^{-2}\right) \tag{11}$$

and

$$h_i = \left(\frac{3!}{n_i!}\right) 2^{3 - 0_i}, \tag{12}$$

α_M is the Madelung constant for the lattice structure, n_i is the number of times any given number occurs in the triplet (x_i, y_i, z_i), 0_i is the number of times that zero occurs in this triplet, and

$$\rho_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}. \tag{13}$$

The wrong expression that Gourary and Adrian obtained instead of Eq. (10) was

$$E_{\mathrm{PI}}^{\mathrm{GA}} = \frac{1}{2a^2}\left\{\xi^2 - \frac{G(\xi)}{\eta}\left[\eta^2 - 3\eta - \frac{1}{2} + \xi^2\left(1 - \frac{1}{\eta} + \frac{1}{2}\eta^{-2}\right)\right]\right\}$$

	ξ	$\bar{T}$	$-\bar{V}_{\rm PI}$	$-E_{\rm PI}^{\rm GA}$	ξ	$\bar{T}$	$-\bar{V}_{\rm PI}$	$-E_{\rm PI}^{b}$
LiF	2.38	0.1774	0.4342	0.2568	2.23	0.1140	0.4113	0.2973
LiCl	2.43	0.1124	0.3439	0.2315	2.31	0.0788	0.3320	0.2532
NaF	2.41	0.1358	0.3789	0.2431	2.28	0.0923	0.3635	0.2712
NaCl	2.45	0.0948	0.3151	0.2203	2.34	0.0685	0.3058	0.2373
KCl	2.47	0.0772	0.2834	0.2062	2.37	0.0574	0.2765	0.2191
RbBr	2.49	0.0653	0.2597	0.1944	2.39	0.0492	0.2538	0.2046

TABLE I. Parameter ξ, kinetic ($\bar{T}$), potential ($\bar{V}_{\rm PI}$) and total ($E_{\rm PI}$) energies for expressions (10) and (14) for six alkali halides. All energies in atomic units.

$$-\frac{1}{a}\left\{\alpha_M - \frac{1}{2}\eta^{-3}G(\xi)\sum_{z_i\geq y_i\geq x_i\geq 0}^{\infty\prime} h_i(-1)^{x_i+y_i+z_i}\frac{(1+\rho_i\xi)}{\rho_i}\exp[-2\eta(\rho_i-1)]\right\}. \quad (14)$$

For completeness, we also give the expression for the first excited state

$$\begin{aligned} E_{\rm PI}^{e} = {} & \frac{1}{2a^2}\Big\{\xi'^2 - 2G'(\xi')\Big[(2\eta')^{-5}(\xi'^2+\eta'^2)\Big[(2\eta')^4 + 4(2\eta')^3 \\ & + 12(2\eta')^2 + 24(2\eta') + 24\Big] - 2(2\eta')^{-3}\Big[(2\eta')^3 + 3(2\eta')^2 + 6(2\eta') + 6\Big]\Big]\Big\} \\ & - \frac{1}{a}\Big\{\alpha_M - \frac{1}{2}\eta'^{-5}G'(\xi')\sum_{z_i\geq y_i\geq x_i\geq 0}^{\infty\prime} h_i(-1)^{x_i+y_i+z_i}\frac{1}{\rho_i} \\ & \times \exp\Big[-2\eta'(\rho_i-1)\Big]\Big[3 + \frac{9}{2}\eta'\rho + 3(\eta'\rho)^2 + (\eta'\rho_i)^3\Big\} \end{aligned} \quad (15)$$

where

$$\begin{aligned} [G'(\xi')]^{-1} = {} & 1 - j_0(\xi')j_2(\xi')[j_1(\xi')]^{-2} \\ & + 2(2\eta')^{-5}[(2\eta')^4 + 4(2\eta')^3 + 12(2\eta')^2 + 24(2\eta') + 24]. \end{aligned} \quad (16)$$

Results and conclusions

We obtained the point-ion approximation and ion-size correction using the correct expression for the energy functional for the ground state wave function of type II (Eq. (10)).

The error in the Eq. (14) is in the kinetic energy ($\bar{T}$). That means that the point-ion potential ($\bar{V}_{\rm PI}$) is the same in Eqs. (10) and (14) for the same ξ. However, the value of x that gives the optimum energy varies if $\bar{T}$ does and consequently $E_{\rm PI}$ varies too.

	$-E_{PI}^{GA}$	$-E_{PI}^{b}$	$-E_{PI}^{GA}$ (III)
LiF	0.2568	0.2973	0.2966
LiCl	0.2315	0.2532	0.2527
NaF	0.2431	0.2712	0.2706
NaCl	0.2203	0.2373	0.2369
KCl	0.2062	0.2191	0.2188
RbBr	0.1944	0.2046	0.2043

TABLE II. Ground state total energies for function of types II and III.

	ξ	$\bar{T}$	$-\bar{V}_P$	$-E_{IS}^{GA}$	ξ	$\bar{T}$	$-\bar{V}_P$	$-E_{IS}^{b}$
LiF	2.46	0.1879	0.4211	0.2332	2.32	0.1308	0.3982	0.2674
LiCl	2.48	0.1166	0.3346	0.2180	2.35	0.0836	0.3210	0.2374
NaF	2.47	0.1419	0.3700	0.2281	2.33	0.0995	0.3524	0.2529
NaCl	2.50	0.0984	0.3083	0.2099	2.36	0.0705	0.2960	0.2255
KCl	2.47	0.0772	0.2815	0.2043	2.36	0.0566	0.2738	0.2172
RbBr	2.45	0.0634	0.2597	0.1963	2.34	0.0458	0.2535	0.2077

TABLE III. Parameter ξ, kinetic ($\bar{T}$), potential ($\bar{V}_P$) and total (E_{IS}) energies that BSG gave in their paper and ours for Eq. (15), with $\alpha = 0.53$.

Table I shows the results obtained by Gourary and Adrian [5] and those obtained with our expression for some alkali halides. We present the different terms that contribute to the total energy. In Table II we compare the results for the wave function of type II and III for the ground state. Gourary and Adrian took the function of type III for the ground state and the function of type II for the first excited state because those functions gave the lowest energies respectively.

Bartram *et al.* took those same wave functions, and they found that good agreement with experimental F-center transition energies could be obtained if all the calculated parameters A_γ were reduced in magnitude by a factor of $\alpha = 0.53$. In table III we show our results taking into account the ion-size approximation with $\alpha = 0.53$ and Eqs. (10) and (14). As we can see in table II the wave function of type II gives lower energy values than type III. Then following the Gourary and Adrian criterion, we can take a wave function of type II (for the ground state) to calculate the transition energy of the F-center. In table IV we compare the transition energies obtained by us with those of other works.

Bartram *et al.* also took into account the polarization energy and distortion of the six nearest neighbours of the F-centers. Weber and Dick [8] used a wave function of type I and a factor $\alpha = 1$ in order to get good agreement with experimental results for F_A-centers. Dochy [12] included polarization energy, lattice distortion, and we present his results where he took a trial wave function of type III for ground state, a function of type II for the excited state and $\alpha = 1$.

We found that values of $\alpha > 0.53$ give lower transition energies than the experimental results.

	Bartram [4] $\alpha = 0.53$	Weber [8] $\alpha = 1$	Dochy [12] $\alpha = 1$	Ours $\alpha = 0.53$	EXP [4]
LiF	0.1930	0.2135	0.2470	0.1875	0.1890
LiCl	0.1210	0.1053	0.1130	0.1178	0.1215
NaF	0.1390	0.1560	0.1860	0.1402	0.1370
NaCl	0.1005	0.0902	0.1080	0.0985	0.1020
KCl	0.0805	0.0916	0.1270	0.0774	0.0860
RbBr	0.0640	0.0717	0.1125	0.0619	0.0680

TABLE IV. Transition energies for six alkali halides given in some works and experimental results.

	Renn [14]	Dochy [12] $\alpha = 1$	Ong-V. [13] $\alpha = 0.53$	Ours $\alpha = 0.53$	Exp. a [4]	Exp. b [4]
LiF	0.1246	0.1990	0.2020	0.1875	0.1885	0.1890
LiCl	0.0978	0.1140	0.1265	0.1178	0.1205	0.1215
LiBr	0.0897	0.0875	0.1090	0.1010	—	0.0995
LiI	0.0798	0.0860	0.0960	0.0888	—	0.1200
NaF	0.1113	0.1600	0.1550	0.1402	0.1380	0.1370
NaCl	0.0871	0.1025	0.1055	0.0985	0.1010	0.1020
NaBr	0.0801	0.0815	0.0940	0.0866	0.0870	0.0865
NaI	0.0720	0.0810	0.0835	0.0773	0.0765	—
KF	0.0937	0.1525	0.1125	0.0978	0.1050	0.1030
KCl	0.0757	0.1030	0.0865	0.0774	0.0845	0.0860
KBr	0.0706	0.0880	0.0780	0.0706	0.0770	0.0765
KI	0.0636	0.0830	0.0705	0.0643	0.0680	0.0690
RbF	0.0875	0.1405	0.0725	0.0780	0.0890	0.0895
RbCl	0.0709	0.1000	0.0735	0.0668	0.0750	0.0745
RbBr	0.0669	0.0865	0.0685	0.0619	0.0680	0.0680
RbI	0.0603	0.0820	0.0630	0.0575	0.0625	0.0630

TABLE V. Transition energies for all alkali halides and experimental results.

Other trial wave functions have been used. Ong and Vail [13] used a Gaussian-localized spherically symmetric wave function and considered the lattice distortion. Dochy [12] included in his work a wave function that is an exact solution for a cuspless hydrogenic potential for the ground state, and for the excited state a type I function with $\alpha = 1$. Renn [14] took Dochy's functions and the theory developed by Stumpf [15]. Brown and Vail [16,17] considered a saddle-point configuration of the F-center using a gaussian-localized wave function. Vail and Harker [18] considered flexible, symmetry-adapted trial pseudowave functions. In table V we compare our results with some of the works that we have described above.

In recent years there have been major developments in the field, namely, the computer analysis of the electronic state from first principles, the application of the method of lattice statics and new methods for taking into account the ionic polarization [19,20,21].

Finally, we notice that the calculated results are closer to experimental results (they do not differ by more than 13%, except for LiI) if one uses trial wave functions of type II and $\alpha = 0.53$ with no polarization nor lattice distortion.

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Resumen. Se calculan las energías de transición para seis halogenuros alcalinos con la aproximación de ion puntual y la corrección de tamaño del ion. Mostramos la expresión correcta para la funcional de la energía con la función tipo II de Gourary y Adrian. Comparamos nuestros resultados con otros trabajos y se encuentra que éstos no difieren más del 13% de los valores experimentales, excepto para LiI, con $\alpha = 0.53$.