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EXCITON IN A RANDOM POTENTIAL

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Экситоны в случайном потенциале

Развита теория поведения экситонов Ванниера-Мотта в случайном потенциале, характеризуемая гауссовым распределением. Получены условия стабильности экситонных состояний, обсуждено расщепление экситонных уровней и проинтерпретированы данные Ca_2O.

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Exciton in a Random Potential

The theory of Wannier-Mott exciton in a random potential with Gaussian distribution functional and with Gaussian correlation functions has been presented for two cases:

1. For the case of $\rho > L - D_e$ the conditions of stability of the exciton have been found.

2. For the case of $\rho < L - D_e$ it has been shown that the influence of the random field on the internal state of the exciton is equivalent to the Stark splitting of the excitonic levels due to an effective Gaussian random electrical field. The theory permits to interpret the experiments of Nikitime et al. on the excitonic absorption spectra of structurally perturbed Cu_2O and to make conclusions about the parameters of the structure of disordered solids (correlation functions, correlation lengths). The respective density of states has been calculated with a strongly marked asymptotic fail behaviour.

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1. INTRODUCTION

The experimental and theoretical investigation of Frenkel excitons in topologically disordered solids shows that the effect of the disorder results in a broadening and shifting of the excitonic spectra by an extent referring to the lifetime broadening [1,2]. On the other hand, the excitons of Wannier-Mott type are very sensitive to the disorder. The experiments of Nikitine et al. [3] demonstrate clearly the sensitivity of the absorption spectra on the mean size L of the "microcrystals". (The conditions of the experiments, $\rho \ll L$, ρ being the exciton diameter, guarantee the relative stability of the exciton). Further experiments of Nikitine et al. [4] show an analogy of the influence of the disorder on the exciton absorption spectra (on the condition $\rho \ll L$, again) to the effects appearing at the application of the electric field on the crystal (Stark effect). Here the decrease of the dimensions of the "microcrystals" has an analogical effect on the exciton absorption spectra as does the increase of the electric field intensity:

1. Shifting of the absorption spectra to the longer wave lengths.

2. Appearance of the new fine structure in some cases.

3. Smoothing of the structure of the spectra beginning with large quantum numbers.

Experiments concerning the optical absorption in amorphous solids show that the most characteristic type of absorption edge is the exponential, i.e., Urbach edge[5]. The theoretical study of the problem of absorption for direct transitions in a uniform electric field by Dow and Redfield[6] has shown that the absorption edge is of Urbach type with the inclusion of the excitonic effects and of Franz-Keldysh type when neglect them. Therefore they propose the unified explanation of the Urbach's rule by the broadening of the excitonic line due to internal electric field of various physical origin (phonons, impurities, defects, etc.)[7]. Proceeding from these results Mott and Davis[5,8] propose the same model for the explanation of the exponential absorption edge in amorphous semiconductors, too, assuming the internal electric fields of about 10^6 - 10^7 Vcm^{-1}. They expect the existence of excitons at least in solids with not too high dielectric constants so that the Coulomb field $e^2/\epsilon\rho$ could lead to bound states as it does in crystals.

The theory presented here proposes the investigation of Wannier excitons in disordered solids by the use of Feynman path integral formalism. This formalism makes averaging procedure relatively simple, but it puts the limiting conditions on the probability distribution functional of the random potential and on the correlation functions. The theory allows us to answer the questions put by Mott and Davis[5], and, namely:

1. The question of stability of the bound state of the electron-hole pair in a random field.

2. The shape of the absorption edge.

3. The expression for the mean-square-root of the internal electric fields in terms of experimental values.

The theory gives, as we shall see, an excellent agreement with the experiments.

2. TWO-PARTICLE DENSITY MATRIX

The motion of a particle in a random potential is a quantum statistical problem, and, therefore, we shall proceed from the quantum statistical density matrix proper to the problem. The two-particle density matrix of the mutually correlated motion of the excited Coulomb bounded electron-hole pair in a thermodynamical equilibrium in a random potential $\eta V(\vec{r})$ is a solution of the Bloch equation

$$-\frac{\partial R}{\partial \beta}=(E_g-\frac{\hbar^2}{2m_e}\Delta_e-\frac{\hbar^2}{2m_h}\Delta_h-\frac{e^2}{\epsilon|\vec{r}_e-\vec{r}_h|}+\eta_e V(\vec{r}_e)+\eta_h V(\vec{r}_h))R. \quad (1)$$

Here $\eta V(\vec{r})$ is a random part of the potential. The periodic part is included in the effective masses m_e , m_h and in the energies E_1, E_2 , $(E_g = E_1 - E_2)$ of the bottom of the conduction band and of the top of the valence band, respectively. $V(\vec{r})$ is a dimensionless function, having the following properties:

$$\langle V(\vec{r})\rangle = 0,$$

$$W(\vec{r}-\vec{r}') = \langle V(\vec{r})V(\vec{r}')\rangle = \exp\{-(\vec{r}-\vec{r}')^2/L^2\}.$$

The solution of eq. (1) averaged over the

Caussian distribution functional $P[V(\vec{r})]$ can be written in the form of the double Feynman path integral

$$<R> = N \int\int D\vec{R}(u)\, D\vec{\rho}(u) \exp(-E_g \beta) \times$$

$$\times \exp\{-\frac{1}{\hbar}\int_0^{\hbar\beta} du\, \frac{1}{2} M \dot{\vec{R}}^2(u) - \frac{1}{\hbar}\int_0^{\hbar\beta} du\,(\frac{1}{2}\mu\dot{\vec{\rho}}^2(u) - \frac{e^2}{\epsilon\,\rho(u)})\} \times \quad (2)$$

$$\times \exp\{\frac{\eta^2}{2\hbar^2}\int_0^{\hbar\beta}\int_0^{\hbar\beta} du'du''[W(\vec{r}_e(u')-\vec{r}_e(u'')) + W(\vec{r}_h(u')-\vec{r}_h(u'')) \pm$$

$$\pm W(\vec{r}_e(u')-\vec{r}_h(u''))]\}.$$

Here $\vec{\rho} = \vec{r}_e - \vec{r}_h$, $\vec{R} = \frac{m_e \vec{r}_e + m_h \vec{r}_h}{M}$.

The sign - (+) pertains to parallelly (anti-parallelly) fluctuating bands, respectively. The correlation length L is supposed to be sufficiently large in order to justify the use of the effective mass approximation in eq. (1) and the use of the harmonic approximation of the correlation function

$$W(\vec{r}-\vec{r}') = 1 - \frac{(\vec{r}-\vec{r}')^2}{L^2}. \quad (3)$$

As it has been pointed out in 10/ namely the quadratic form of the correlation functions enables one to calculate the Feynman path integral analytically. (The diffusion lengths $D = (\frac{2\hbar^2\beta}{m})^{1/2}$ of both particles are supposed to satisfy the relation $D < L$).

The arguments of the mixed correlation functions $W(\vec{r}_e(u')-\vec{r}_h(u''))$ satisfy the inequality

$$|\vec{r}_e(u')-\vec{r}_h(u'')| \le |\vec{r}_e(u')-\vec{r}_e(u'')| + |\vec{\rho}(u'')| \le D^e + \rho(u'').$$

Further, we can distinguish two cases:

a) $D^e + \rho(u) \ge L$,

b) $D^e + \rho(u) < L$.

If the radius of the exciton ρ is sufficiently large in order to satisfy the relation a) the mixed correlation is negligibly small,

$$W(\vec{r}_e(u')-\vec{r}_h(u'')) = \exp(-\frac{(\vec{r}_e(u')-\vec{r}_h(u''))^2}{L^2}) \ll 1,$$

and we neglect it in eq. (2).

3. THE CASE OF LARCE EXCITON RADIUS, $\rho \ge L - D_e$ /9/.

3.1. The Averaged Two-Particle Density Matrix

For further calculations it is useful to introduce the mean frequency of the hydrogen-like internal motion of the exciton in the stationary state ω_c by the condition of the mechanical equilibrium

$$\frac{e^2}{\epsilon\,\rho(u)} = \frac{1}{2}\mu\omega_c^2\rho^2(u). \quad (4)$$

The expression for the averaged density matrix can be then written in the form

$$<R(\vec{R},\vec{R}^\circ,\vec{\rho},\vec{\rho}^\circ,\beta)> = N\exp\{\eta^2\beta^2 - E_g\beta\}\times$$

$$\times \int D(\vec{R}(u))\exp\{-\frac{M}{2\hbar}\int_0^{\hbar\beta}\dot{\vec{R}}^2(u)\,du - \frac{\eta^2}{\hbar^2 L^2}(1-\frac{a}{2})\int_0^{\hbar\beta}\int_0^{\hbar\beta} du'du''\times$$

$$\times(\vec{R}(u')-\vec{R}(u''))^2\, J(\vec{R}(u),\vec{\rho},\vec{\rho}^\circ,\beta),$$

where

$$J(\vec{R}(u),\vec{\rho},\vec{\rho}^{\circ},\beta)=\int D\vec{\rho}(u)\exp\{-\frac{\mu}{2h}\int_0^{\hbar\beta}(\dot{\vec{\rho}}^2(u)+\omega_c^2\rho^2(u))\,du$$

$$-\frac{\eta^2}{2\hbar^2L^2}(a^2+b^2)\int_0^{\hbar\beta}\int_0^{\hbar\beta}(\vec{\rho}(u')-\vec{\rho}(u'')-a\vec{R}(u')+a\vec{R}(u''))^2\,du'du''. \quad (6)$$

Here $a=\frac{a-b}{a^2+b^2}$, $a=\frac{m_h}{M}$, $b=\frac{m_e}{M}$.

The path integrals in (5) separate accurately, or, in other words, the internal motion and the motion of two mass center become independent, if

a) $a=0$ $(m_e=m_h)$,

b) $\vec{R}\approx\text{const}$ $(m_e\ll m_h\approx M)$.

Therefore, the coupling of both motions depends on the relation of the effective masses. Let us suppose a to be small, $a^2\approx 0$. Then, both motions in the expression (5) can be separated approximately as

$$<R_\beta(\vec{R},\vec{R}^{\circ},\vec{\rho},\vec{\rho}^{\circ})>\simeq\exp\{-\beta E_g+\eta^2\beta^2\}<R_\beta(\vec{R},\vec{R}^{\circ})>\times$$
$$\times<R_\beta(\vec{\rho},\vec{\rho}^{\circ},a\vec{R},a\vec{R}^{\circ})>, \quad (7)$$

where

$$<R_\beta(\vec{R},\vec{R}^{\circ})>=N_1\int D\vec{R}(u)\exp\{\frac{S(\vec{R},\vec{R}^{\circ},\beta)}{h}\}$$

$$<R_\beta(\vec{\rho},\vec{\rho}^{\circ},a\vec{R},a\vec{R}^{\circ})>=N_2\int D\vec{\rho}(u)\exp\{\frac{S(\vec{\rho},\vec{\rho}^{\circ},a\vec{R},a\vec{R}^{\circ})}{h}\}.$$

Here, the corresponding actions are

$$S(\vec{R},\vec{R}^{\circ},\beta)=-\frac{M}{2\hbar}\int_0^{\hbar\beta}\dot{\vec{R}}^2(u)du-\frac{\eta^2}{\hbar^2L^2}(1-\frac{a}{2})\int_0^{\hbar\beta}\int_0^{\hbar\beta}(\vec{R}(u')-\vec{R}(u''))^2\,du'du'' \quad (8)$$

and

$$S(\vec{\rho},\vec{\rho}^{\circ},a\vec{R},a\vec{R}^{\circ},\beta)=-\frac{M}{2\hbar}\int_0^{\hbar\beta}\dot{\vec{\rho}}^2(u)\,du-\frac{1}{2\hbar}\mu\omega_c^2\int_0^{\beta}\rho^2du-$$
$$-\frac{\eta^2}{2\hbar^2L^2}(a^2+b^2)\int_0^{\hbar\beta}\int_0^{\hbar\beta}[(\vec{\rho}(u')-\vec{\rho}(u''))^2-2a(\vec{\rho}(u')-\vec{\rho}(u''))\times \quad (9)$$
$$\times(\vec{R}(u')-\vec{R}(u''))]du'du''.$$

3.2. Effective Hopping Motion of the Mass Center

The problem of the center-of-mass motion, as can be seen from (8) reduces to the problem of a harmonic oscillator with memory, which appears at the investigation of a single particle in a Gaussian random potential. This problem has been solved by Bezak[10], Barta[11] and Papadopoulos[12].

Proceeding from the principle of the minimum action, $\delta S(\vec{R},\vec{R}^{\circ},\beta)=0$, we obtain the solution for $\vec{R}(u)$

$$\vec{R}(u)=\frac{1}{2}(\vec{R}+\vec{R}^{\circ})+\frac{1}{2}(\vec{R}-\vec{R}^{\circ})\frac{\sinh[\Omega(u-\frac{1}{2}\hbar\beta)]}{\sinh(\frac{\Omega\hbar\beta}{2})},$$

where $\vec{R}=\vec{R}(\hbar\beta)$, $\vec{R}^{\circ}=\vec{R}(0)$.

The corresponding action is

$$S(\vec{R},\vec{R}^{\circ},\beta)=-\frac{1}{2\hbar^2\beta}M_G(\vec{R}-\vec{R}^{\circ})^2,$$

where

$$M_G=\frac{1}{2}M\beta\hbar\Omega\coth(\frac{1}{2}\beta h\Omega), \quad (10)$$

and

$$\Omega=\frac{2\eta}{L}(1-\frac{a}{2})^{1/2}(\frac{\beta}{M})^{1/2}. \quad (11)$$

Here we have introduced, analogically as in[10], the "second effective mass" M_G giving

the measure of localization of the mass center. Namely, if $T \to 0$, then $\Omega \to \omega$, $M_G \to \infty$ (perfect localization); if $T \to \infty$, $\Omega \to 0$, $M_G \to M$ (quasifree motion). Ω has a meaning of the mean frequency of the mass centers in the potential wells. The coupling of the mass center motion with the internal motion appearing in the expressions (10) and (11) through α diminishes the localization (i.e., Ω and M_G) of the mass center (in most cases $\alpha > 0$) and, therefore, contributes to the scattering of the internal bound state (conservation of energy).

3.3. Effective Internal Motion of the Pair in a Quasiclassical Picture

The exact solution for the "classical path" of the excitation radius can be obtained by a similar way as in the proceeding section.

It reads

$$\vec{\rho}(u) = \frac{1}{2}(\vec{\rho}+\vec{\rho}^{\circ})\,F(\omega) + [\vec{\rho} - \frac{1}{2}(\vec{\rho}+\vec{\rho}^{\circ})\,F(\omega)]\frac{\mathrm{sh}(\phi u)}{\mathrm{sh}(\phi\hbar\beta)} +$$

$$[-\vec{\rho}^{\circ} + \frac{1}{2}(\vec{\rho}+\vec{\rho}^{\circ})\,F(\omega)]\frac{\mathrm{sh}(\phi(u-\hbar\beta))}{\mathrm{sh}(\phi\hbar\beta)} + \qquad (12)$$

$$+ \frac{a\omega^2}{2}\frac{(\vec{R}-\vec{R}^{\circ})}{\Omega^2-\phi^2}\left[\frac{\mathrm{sh}(\Omega(u-\frac{\hbar\beta}{2}))}{\mathrm{sh}(\frac{\Omega\hbar\beta}{2})} - \frac{\mathrm{sh}(\phi(u-\frac{\hbar\beta}{2}))}{\mathrm{sh}(\frac{\phi\hbar\beta}{2})}\right].$$

Here $\vec{\rho} = \vec{\rho}(\hbar\beta)$, $\vec{\rho}^{\circ} = \vec{\rho}(0)$,

$$\omega^2 = \frac{2\eta^2\beta(a^2+b^2)}{\mu L^2}, \quad \phi^2 = \omega^2 - \omega_c^2, \qquad (13)$$

ω_c is defined by eq. (4).

Further,

$$F(\omega) = \left(1 - \frac{\omega_c^2}{2\omega^2}\,\frac{\phi\hbar\beta}{\mathrm{th}\,\frac{\phi\hbar\beta}{2}}\right)^{-1} \qquad \text{for } \omega > \omega_c \qquad (14)$$

and

$$F(\omega) = \left(1 - \frac{\omega_c^2}{2\omega^2}\,\frac{\Phi\hbar\beta}{\mathrm{tg}\,\frac{\Phi\hbar\beta}{2}}\right)^{-1}, \quad \Phi = (\omega_c^2 - \omega^2)^{1/2} \qquad (15)$$

$$\text{for } \omega < \omega_c .$$

The analysis of the function $F(\omega)$, determining the dispersion of the internal state (eq. (12)) shows [9] that

$$\lim_{\omega \to \omega_c} F(\omega) \to \infty \qquad \text{and} \quad |\rho| \to \infty$$

$$\lim_{\omega \to 0} F(\omega) = 0 \qquad \text{and} \quad \rho \to \rho_c .$$

In view of this and of the analysis of respective actions for the regions $\omega < \omega_c$ and $\omega > \omega_c$ [9] we can conclude the following:

a) At the resonant frequency $\omega = \omega_c$ the dissociation appears.

b) If the Coulomb interaction dominates, i.e., if the relations

$$\omega^2 < \omega_c^2 \qquad (16a)$$

or, equivalently,

$$\frac{\eta^2\beta}{L^2}\,\frac{m_e^2 + m_h^2}{M^2} < \frac{e^2}{\epsilon\,\rho^3(u)} \le \frac{e^2}{\epsilon\,L^3} \qquad (16b)$$

hold, the internal motion keeps a hydrogen-like character with the frequency $\Phi = (\omega_c^2 - \omega^2)^{1/2}$. The relations (16) give the criteria of stability of the electron-hole pair, which

complete and precise the criterion of Rice and Jortner $r_c < r_D$ /13/ , $r_c \sim 1/\omega_c$, $r_D \sim 1/\omega$.

c) If $\omega^2 > \omega_c^2$, the bound state of the pair is destroyed by the disorder (the Coulomb interaction is exceeded by the scattering influence of the disorder). The electron is localized "during the period of its motion around the hole r_c, $r_c > r_D$.

Hence, the character of the internal motion is determined by the dominancy of one of the two interactions as discussed above.

4. THE CASE OF "SMALL" EXCITON RADIUS, $\rho < L - De$

4.1. Stark Effect Due to Disorder

In this case the mixed correlation function $W(\vec{r}_e - \vec{r}_h)$ has to be taken into account in eq. (2). Moreover, the condition $\rho < L - De$ makes possible the use of the harmonic approximation (3) for $W(\vec{r}_e - \vec{r}_h)$, too.

So the correlation term in (2) turns out to be

$$\exp\{\frac{\eta^2}{2\hbar^2}\int_0^{\hbar\beta}\int_0^{\hbar\beta} du'du''[W(\vec{r}_e(u') - \vec{r}_e(u'')) + W(\vec{r}_h(u') - \vec{r}_h(u'')) - 2W(\vec{r}_e(u') - \vec{r}_h(u''))]\} = \exp[\frac{\eta^2}{\hbar^2 L^2}\sum_{i=1}^{3}(\int_0^{\hbar\beta} du\, \rho^{(i)}(u))^2], \quad (17)$$

where $\rho^{(i)}(u)$, $i = 1,2,3$ are the components of the relative coordinate $\vec{\rho}(u) = \vec{r}_e(u) - \vec{r}_h(u)$.

The expression in the exponential in (17) can be linearized by the transformation

$$\int_{-\infty}^{\infty} \exp(-\frac{q^2}{4} - iMq)\, dq = 2\sqrt{\pi}\exp(-M^2) \quad (18)$$

with

$$M^{(j)2} = -\frac{\eta^2}{\hbar^2 L^2}(\int_0^{\infty} du\, \rho^{(j)}(u))^2 , \quad j = 1,2,3, \quad (19)$$

as follows

$$\frac{1}{(2\sqrt{\pi})^3}\int_{-\infty}^{\infty}\int dq_1 dq_2 dq_3 \exp(-\frac{1}{4}(q_1^2 + q_2^2 + q_3^2))\exp(\frac{1}{\hbar}\int_0^{\hbar\beta} e\vec{F}\cdot\vec{\rho}(u)\, du). \quad (20)$$

Here

$$\vec{F} = \frac{\eta}{eL}\vec{q} \quad (21)$$

is the induced effective stochastical electrical field depending on the parameters η, L characterizing the "randomness" of the solid and on the stochastical parameters q with the induced Gaussian distribution function $\frac{1}{(2\sqrt{\pi})}\exp[-\frac{1}{4}(q_1^2 + q_2^2 + q_3^2)]$. This "random internal electric field representation" has been firstly introduced in this way by Barta/11/ Hence, the random electric field representation of the density matrix reads

$$\langle R \rangle = \exp(-\beta E_g)R(\vec{R}, \vec{R}^\circ, \beta)\frac{1}{(2\sqrt{\pi})^3}\int_{-\infty}^{\infty}\int R(\vec{\rho}, \vec{\rho}^\circ, \beta, \vec{q}) \times \exp(-\frac{q^2}{4})\prod_{i=1}^{3} dq_i , \quad (22)$$

where

$$R(\vec{R}, \vec{R}^\circ, \beta) = (\frac{M}{2\pi\hbar^2\beta})^{3/2}\exp(-\frac{M}{2\hbar^2\beta}(\vec{R} - \vec{R}^\circ)^2) \quad (23)$$

and

$$R(\vec{\rho}, \vec{\rho}^\circ, \beta, \vec{q}) = \int D\vec{\rho}(u)\, \exp\{-\frac{1}{\hbar}\int_0^{\hbar\beta}[\frac{1}{2}\mu\dot{\vec{\rho}}^2(u) - \frac{e^2}{\epsilon\rho(u)} - e\vec{F}\cdot\vec{\rho}(u)]\, du\}.$$

The last quantity can be interpreted as a probability density of the density matrix of the exciton in a random electric field $\vec{F}$. Providing Boltzman statistics it can be written in a common way as

$$R(\vec{\rho},\vec{\rho}^{\circ},\beta,\vec{q}) = \sum_i \Phi_i^*(\vec{\rho},\vec{q})\,\Phi_i(\vec{\rho}^{\circ},\vec{q})\,\exp(-\beta E_i(\vec{q})) . \qquad (25)$$

Obviously, Φ_i , E_i are the solutions of the "local" Schroedinger equation

$$\left[-\frac{\hbar^2}{2\mu}\Lambda_\rho - \frac{e^2}{\epsilon\,\rho(u)} - e\vec{F}(\vec{q})\,\vec{\rho}\right]\Phi_i(\vec{\rho},\vec{q}) = E_i(\vec{\rho},\vec{q})\,\Phi_i(\vec{\rho},\vec{q}) . \qquad (26)$$

This is the equation describing the hydrogenlike motion in the electric field $\vec{F}(\vec{q})$. So we come to the statement: If the radius of the exciton ρ satisfies the relation $\rho <$ L-De, then the effect of the disorder on the internal structure of the exciton is equivalent to the Stark splitting of the excitonic spectra in the crystal due to the electrical field $\vec{F}(\vec{q})$ and has to appear in the absorption spectra. This effect has been really observed by Nikitine et al. /4/ for the yellow series of Cu_2O, as has been mentioned in the Introduction. The disorder has been achieved by the irradiation of the crystalline Cu_2O by protons and neutrons and the characteristic length has been estimated to be ~75Å. As the Bohr radius of the lowest exciton state in Cu_2O is ~10Å , the condition needed for the appearance of the effect has been satisfied. With the increasing intensity of bombarding particles the structure of the spectra become less distinct and lastly disappeared. This smoothing of the spectra can be explained by the decrease of L with the increase of the intensity of the particles. Then the radius ρ becomes comparable with L, $L \to \rho + De$ and we come to the case of $\rho > L - De$ which has been discussed in Sect.3

This effect of smoothing begins, obviously, from the large quantum numbers, as it has been really observed /3,4/.

4.2. The Density of States

The density of states is given by the equation

$$n(E) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty du\,\exp[(iE-\epsilon)u]\,Z(iu) , \qquad (27)$$

where the partition function

$$Z(iu) = \frac{1}{V^2}\iint d\vec{R}\,d\vec{\rho}\,\langle R_{iu}(\vec{R},\vec{\rho})\rangle , \quad iu = \beta \qquad (28)$$

is expressed through the diagonal elements of the density matrix (22)

$$\langle R_\beta(\vec{R},\vec{\rho})\rangle = \left(\frac{M}{2\pi\hbar^2\beta}\right)^{3/2}\frac{\exp(-E_g\beta)}{(2\sqrt{\pi})^3}\iiint_{-\infty}^{\infty} e^{-\frac{q^2}{4}} R(\vec{\rho},\vec{q},\beta)\,dq . \qquad (29)$$

The favourable way of finding the quantity $R(\vec{\rho},\vec{q},\beta)$ gives eqs. (25) and (26).

The orientation of the electrical field $\vec{F}(q)$ is determined by the parameters q_i (21) and, generally, $q_i \neq 0$, $i = 1,2,3$. So we have to perform a transformation of the coordinate system in order to have the orientation of the Z-axis along the vector $\vec{F}$. For simplicity and for the possibility of application to the case of Cu_2O we shall choose the lowest excited state $n = 2$. After rather long calculations (details are given in /14/) one obtains finally the following expression for the density of states

$$n(E) = \frac{4}{\sqrt{\pi}}\left(\frac{M}{2\pi\hbar^2}\right)^{3/2} \mathrm{Re}\left[(E-E_g-E_2^\circ)^{1/2}\right] +$$

$$+ \frac{5}{3\sqrt{\pi}}\left(\frac{M}{2\pi\hbar^2}\right)^{3/2} d^{1/2} \exp\left[-\frac{(E-E_g-E_2^\circ)^2}{4d^2}\right] \times \qquad (30)$$

$$\times \mathrm{Re}\left(i^{1/2}\left\{D_{1/2}\left(-\frac{i(E-E_g-E_2^\circ)}{d}\right) + \frac{1}{4} D_{-3/2}\left(-\frac{i(E-E_g-E_2^\circ)}{d}\right)\right.\right.,$$

where $d = \frac{3a}{L}\eta$, D_ν are parabolic cylinder functions.

The first term in expression (30) is the density of states related to the free m motion of the mass center and to the unperturbed internal bound state with the energy E_2°. It is non-zero if $E - E_g - E^\circ_2 > 0$. The second term relates to the effect of disorder. Its role becomes more evident from the asymptotic behaviour of the function $n(E)$:

a) For $E-E_g-E_2^\circ \gg \frac{3a}{L}\eta$

we obtain

$$n(E) \sim \frac{4}{\sqrt{\pi}}\left(\frac{M}{2\pi\hbar^2}\right)^{3/2} (E-E_g-E_2^\circ)^{1/2} + \frac{5}{3\sqrt{\pi}}\left(\frac{M}{2\pi\hbar^2}\right)^{3/2} \times$$

$$\times\left[(E-E_g-E_2^\circ)^{1/2} - \frac{3}{8}\frac{d^2}{(E-E_g-E_2^\circ)^{3/2}}\left(1+O\left(\frac{d^2}{(E-E_g-E_2^\circ)^2}\right)\right)\right] \qquad (31)$$

b) For $|E-E_g-E_2^\circ| \gg \frac{3a}{L}\eta$, $E-E_g-E_2^\circ < 0$

we have a "tail" behaviour as

$$n(E) = \frac{5}{6}\sqrt{\frac{2}{\pi}}\left(\frac{M}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{(E-E_g-E_2^\circ)^2}{2d^2}\right) \times$$

$$\times\left\{|E-E_g-E_2^\circ|^{1/2} + \frac{9}{8}\frac{d^2}{|E-E_g-E_2^\circ|^{3/2}}\left(1+O\left(\frac{d^2}{|E-E_g-E_2^\circ|^2}\right)\right)\right\}. \qquad (32)$$

From the last formula we can conclude the following:

1. The tail part, i.e., the range of $n(E) \neq 0$ for $E-E_g-E_2^\circ<0$ increases with increasing $d=3a\eta/L$. These states take part in the optical absorption and so the absorption edge shifts to longer wave lengths. This shifting has been observed by Nikitine et al.[3,4]
2. In the range $E' = E-E_g-E_2^\circ < 0$ a new maximum of the density of states may appear which will shift to smaller energies with increasing d. This effect might cause the doubling of absorption lines[3,4].

The agreement of our results with the experimental results of Nikitine et al.[3,4] allows us to conclude that the proposed model (Caussian distribution functional of the random potential $V(\vec{r})$ and the Caussian form of the correlation functions) seems to be reasonable.

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