ELECTRON LOCALIZATION IN CLUSTERS SUBJECT TO A STRONG MAGNETIC FIELD

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An electron is shown to localize in a strong magnetic field at the cluster with the number of molecules less than the critical one, which is impossible in the absence of the field. For the subcritical ammonium cluster with n=8 and magnetic field $H \approx 10^5$ Oe, the electron photodetachment energy is 10^{-3} eV.
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1. Introduction

In the present paper we consider properties of a charged cluster of polar molecules in a strong magnetic field. If the number of cluster molecules is rather large, the cluster can be considered as a dielectric sphere. Then electron localization at the cluster results from attraction of the electron by the sphere and formation of the polaron state. This mechanism was considered in [1-3], in particular, to show the existence of a critical sphere size R_c at which the polaron state arises.

Below we demonstrate that a strong magnetic field localizes the electron at the cluster. In particular, the electron state bound to the cluster is possible for subcritical clusters in the strong field.

2. Cluster in a magnetic field

The electron energy W in the cluster subject to a magnetic field is determined by the Schrodinger equation

$$\frac{\left(\hat{P} + e/c\, A\right)^2}{2\mu}\psi - e\varphi\psi = W\psi\,, \tag{1}$$

where μ is the effective electron's mass, $\hat{P}$ is its momentum, A is the vector potential, and $\varphi(r)$ is the potential of cluster polarization. According to the polaron model, the latter takes on the form

$$\varphi(r) = \frac{e}{\tilde{\varepsilon}}\int \frac{|\psi(r')|^2}{|r - r'|}\, d\upsilon' - c\,, \tag{2}$$

where $\tilde{\varepsilon}^{-1} = \varepsilon_\infty^{-1} - \varepsilon_0^{-1}$ is the effective dielectric constant, ε_∞, and ε_0 are the high-frequency and static dielectric constants, and c is the constant determined by vanishing the potential outside the cluster. Using the cylindrical coordinates and symmetrical calibration for the vector potential, A_x = -HY/ 2, A_y = HX / 2, and A_z = 0, we have

$$\frac{\left(\hat{P} + \frac{e}{c}A\right)^2}{2\mu} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right) + \frac{\partial^2}{\partial Z^2} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}\right] + i\frac{\hbar^2}{2\mu\rho_0^2}\frac{\partial}{\partial\varphi} + \frac{\hbar^2}{2\mu\rho_0^2}\left(\frac{\rho}{2\rho_0}\right)^2, \tag{3}$$

where $\rho_0 = \sqrt{\frac{c\hbar}{eH}}$ is the effective magnetic length. The eigenfunctions in the right side of (3) are expressed in the cylindrical coordinates by

$$\psi_{N,m,K_z}(r) = \frac{\exp(iK_z z)}{\sqrt{L}} \frac{\exp(-im\varphi)}{\sqrt{2\pi}} \frac{1}{\rho_0} \times \left(\frac{n!}{(n+|m|)!}\right)^{1/2} \times$$
$$\times \exp\left(-\rho^2/4\rho_0^2\right)\left(\frac{\rho^2}{2\rho_0^2}\right)^{|m|/2} L_n^{(|m|)}\left(\frac{\rho^2}{2\rho_0^2}\right), \tag{4}$$

where m is the projection of the electron orbital momentum onto the magnetic field direction, n=N+1/2(m—|m|), and $L^{(m)}{}_n$ are the Laguerre polynomials. The value n can be shown to be positive and m > -N. For the lowest Landau band with n = N = 0, the wave function (4) is given by

$$\psi(r) = R_{00}(\rho)\chi(Z), \tag{5}$$

$$R_{00}(\rho) = \frac{1}{\sqrt{2\pi}\rho_0} \exp\left(-\rho^2/4\rho_0^2\right). \tag{6}$$

3. Cluster in a quantizing magnetic field

The potential well produced by the cluster polarization in magnetic field is axially symmetrical. Hence, m is the quantum number of the problem and m=0 corresponds to the electron ground state. Below we consider the limiting quantizing magnetic field when $\hbar\omega_H > |W|$, where $\omega_H = eH/\mu c$ is the frequency of the lowest Landau level. In this limit, the wave function determined by (5) and (6) is the asymptotically exact solution to problem (1). Substituting (5) and (6) into (1), multiplying equation (1) by $2\pi\rho R_{00}(\rho)$, and integrating it over ρ, we have the Schrodinger equation for $\chi(Z)$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(Z)}{dZ^2} - e\overline{\varphi}(Z)\chi(Z) = W\chi(Z), \tag{7}$$

where

$$e\overline{\varphi}(Z) = 2\pi\frac{e^2}{\widetilde{\varepsilon}} \int\limits_{\rho',Z'\in V',\rho,Z\in\Omega} \frac{\chi^2(Z')R_{00}^2(\rho')R_{00}^2(\rho)\rho\rho' d\rho\, d\rho' dZ' d\varphi'}{\sqrt{(\vec{\rho}-\vec{\rho}')^2+(Z-Z')^2}} - c\,. \tag{8}$$

and respectively

$$e\overline{\varphi}(Z) = 0\,, \quad \rho\,, \quad Z\notin\Omega\,. \tag{9}$$

We integrate (8) over ρ' and Z' in the whole space, while over ρ and Z only inside the cluster. The constant c is determined by continuity of $\varphi(Z)$ at the cluster surface. As it follows from (6) and (8), in the limit of superstrong magnetic field, as $\rho_0 \to 0$, we have

$$\lim_{\rho_0\to 0} e\overline{\varphi}(Z) = \frac{e^2}{\widetilde{\varepsilon}} \int\limits_{-\infty}^{\infty} \frac{\chi^2(Z')dZ'}{\sqrt{\xi_1\rho_0^2+(Z-Z')^2}} - c\,, \tag{10}$$

where ξ_1 is a number of the order of unity. Solving the Schrodinger equation (7) with potential (10) is a complicated problem. To find the solution, we use a variational approach. Taking the asymptotics

$$2\int\limits_{-\infty}^{\infty} \frac{\chi^2(z')dz'}{\sqrt{\xi_1\rho_0^2+(Z-Z')^2}} \geq \sqrt{\xi_1}\,\rho_0 \int\limits_{-\infty}^{\infty} \frac{\chi^2(Z')dZ'}{\xi_1\rho_0^2+(Z-Z')^2} \xrightarrow[\rho_0\to 0]{} \pi\int\limits_{-\infty}^{\infty}\delta(Z-Z')\chi^2(Z')dZ' = \pi\chi^2(Z) \tag{11}$$

we use a shallow well $e\overline{\varphi}(z)$ for which $|e\overline{\varphi}_1(z)| < |e\overline{\varphi}(z)|$, instead of the potential well $e\overline{\varphi}_1(z)$. As it follows from (10) and (11), we can choose

$$e\overline{\varphi}_1(Z) = \frac{\pi}{2}\frac{e^2}{\widetilde{\varepsilon}}\left[\chi^2(Z) - \chi^2(R)\right], \tag{12}$$

where R is the cluster radius.

4. Dimensionless nonlinear cluster equations

Substituting (12) into (7), we arrive at the approximate equations for an electron in the cluster subject to the quantizing field

$$\begin{aligned} &\frac{d^2\chi(Z)}{dZ^2} + \pi\frac{\mu e^2}{\widetilde{\varepsilon}\hbar^2}\left[\chi^2(Z) - \chi^2(R)\right]\chi(Z) + \frac{2\mu}{\hbar^2}W\chi(Z) = 0, \quad |Z| < R; \\ &\frac{d^2\chi(Z)}{dZ^2} + \frac{2\mu W}{\hbar^2}\chi(Z) = 0, \quad |Z| > R, \end{aligned} \tag{13}$$

$$\int_{-\infty}^{\infty}\chi^2(Z)dZ = 1. \tag{14}$$

Using the scaling

$$\chi(Z) = \sqrt{\frac{2\widetilde{\varepsilon}|W|}{\pi e^2}}\,Y(\widetilde{Z}), \tag{15}$$

$$Z = \sqrt{\frac{\hbar^2}{2\mu|W|}}\,\widetilde{Z}, \tag{16}$$

we have instead of (13) the dimensionless equations

$$\begin{aligned} &Y''(\widetilde{Z}) + \left[Y^2(\widetilde{Z}) - Y^2(\xi_0)\right]Y(\widetilde{Z}) - Y(\widetilde{Z}) = 0, \qquad |\widetilde{Z}| \le \xi_0, \\ &Y''(\widetilde{Z}) - Y(\widetilde{Z}) = 0, \qquad |\widetilde{Z}| > \xi_0, \end{aligned} \tag{17}$$

where

$$\xi_0 = R\sqrt{\frac{2\mu|W|}{\hbar^2}}. \tag{18}$$

The electron energy is found from normalizing condition (14). Substituting (15) and (16) into it, we have

$$W = -\frac{\pi^2}{2\Gamma^2}\frac{e^4\mu}{\widetilde{\varepsilon}^2\hbar^2}, \tag{19}$$

where

$$\Gamma = \int_{-\infty}^{\infty}Y^2(\widetilde{Z})d\widetilde{Z}. \tag{20}$$

Thus, according to (19) and (20), the electron energy is calculated by integral (20), using the solution to (17). As it follows from (18) and (19), there is a relation between ξ_0 and Γ

$$\Gamma \xi_0 = \pi \frac{e^2 \mu R}{\widetilde{\varepsilon} \hbar^2} . \tag{21}$$

5. Asymptotic solutions to equations (17)

We consider the case of a shallow well, i.e.,

$$\frac{\hbar^2}{\mu R^2} >> |W| . \tag{22}$$

that corresponds to

$$\xi_0 << 1 . \tag{23}$$

men we nave the followin asymptotics under condition (23) (see Appendix)

$$Y\left(\widetilde{Z}\right) \approx \frac{c}{\xi_0}, \quad c = \frac{\pi}{2\sqrt{2}}, \quad \left|\widetilde{Z}\right| \le \xi_0 . \tag{24}$$

The parameter Γ can be directly calculated by (20). Taking into account the small ξ_0, we deduce

$$\Gamma = \int_{-\infty}^{\infty} Y^2\left(\widetilde{Z}\right) d\widetilde{Z} \approx Y^2(0) \int_{-\infty}^{\infty} e^{-2|\widetilde{Z}|} d\widetilde{Z} = Y^2(0). \tag{25}$$

where according to (17) we assume the solution to take on the form $Y(\widetilde{Z}) = Y(\xi_0) \exp(-\widetilde{Z} + \xi_0)$, $\widetilde{Z} > \xi_0$ in the whole range of $\widetilde{Z}$ except for a narrow interval $|\widetilde{Z}| < \xi_0$ Comparing (24) and (25), we arrive at

$$\Gamma = \frac{c^2}{\xi_0^2} . \tag{26}$$

Further, using (21) and (26), we find

$$\xi_0 = \frac{c^2}{\pi} \frac{\widetilde{\varepsilon} \hbar^2}{e^2 \mu R} . \tag{27}$$

and the electron energy is given by

$$W = -\frac{c^4}{2\pi^2} \frac{\widetilde{\varepsilon}^2 \hbar^6}{e^4 \mu^3 R^4} . \tag{28}$$

which can be transformed into

$$W = -\frac{c^4}{2\pi^2} \frac{\widetilde{\varepsilon}^2 \hbar^2}{m_0 a_B^2} \left(\frac{a_B}{R}\right)^4 \left(\frac{m_0}{\mu}\right)^3 , \tag{29}$$

where $a_B = \hbar^2 / m_0 e^2$ is the Bohr radius.

As it follows from (16) and (27), the typical electron size r_z (the scale factor for dimension-less

variable $\widetilde{Z}$) is expressed by

$$r_Z = \frac{\pi}{c^2} R^2 \frac{\mu e^2}{\hbar^2 \widetilde{\varepsilon}}. \tag{30}$$

or by

$$r_Z = \frac{\pi}{c^2} \frac{R}{\widetilde{\varepsilon}} \left(\frac{R}{a_B} \right). \tag{31}$$

Next we consider the case of a deep well, when

$$|W| >> \frac{\hbar^2}{\mu R^2}. \tag{32}$$

Neglecting $x(R)$ in (13), we find from (17) that

$$\Gamma \to 4, \text{ as } \xi_0 \to \infty. \tag{33}$$

Thus, in this limit the electron energy is given by

$$W = -\frac{\pi^2}{32} \frac{e^4 \mu}{\widetilde{\varepsilon}^2 \hbar^2}. \tag{34}$$

while according to (16) the typical electron size takes on the form

$$r_Z = \frac{4}{\pi} \frac{\hbar^2 \widetilde{\varepsilon}}{\mu e^2}. \tag{35}$$

6. Numerical solution to problem (17)

Equation (17) can be numerically integrated. It has only one parameter

$$\kappa = \Gamma \xi_0 = \pi \varepsilon \frac{e^2 R \mu}{\widetilde{\varepsilon} \hbar^2}. \tag{36}$$

The values of Γ and ξ_0 are determined by (21) and by continuity of $Y(\widetilde{Z})$ at $|\widetilde{Z}| = \xi_0$. Figure 1 plots solutions to (17) at various κ.

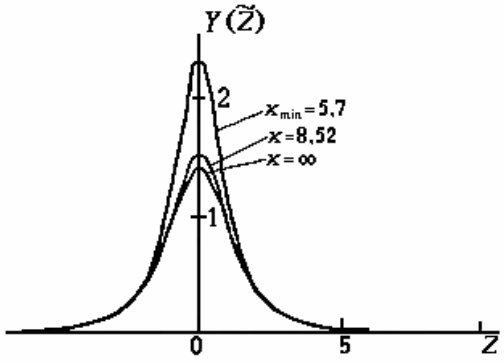

Figure 1. Solutions to Eqs. (17) at different κ

By the solutions found, we can calculate the total electron energy determined by the functional

$$F = \frac{\hbar^2}{2\mu}\int_{-\infty}^{\infty}\chi'^2 d\,Z \;-\; \frac{\pi}{4}\,\frac{e^2}{\widetilde{\varepsilon}}\int_{-R}^{R}\chi^4 d\,Z \;+\; \frac{\pi}{4}\,\frac{e^2}{\widetilde{\varepsilon}}\,\chi^2(R)\int_{-R}^{R}\chi^2 d\,Z\,. \tag{37}$$

Note that equations (13) result from varying the functional F with respect to wave function χ. Using (15) and (16), we express the total energy

$$F = \frac{\pi^2}{2}\,\frac{\mu e^4}{\widetilde{\varepsilon}^2\hbar^2}\,\frac{\overline{F}}{\Gamma^3}\,, \tag{38}$$

where

$$\overline{F} = \int_{-\infty}^{\infty} Y'^2 d\,\widetilde{Z} - \frac{1}{2}\int_{-\xi_0}^{\xi_0} Y^4 d\,\widetilde{Z} + \frac{1}{2}\,Y^2(\xi_0)\int_{-\xi_0}^{\xi_0} Y^2 d\,\widetilde{Z}\,. \tag{39}$$

We also find the effective electron radius

$$\langle r\rangle = \int_0^{\infty} Z\,\chi^2(Z) d\,Z\,, \tag{40}$$

as

$$\langle r\rangle = \frac{\widetilde{\varepsilon}\,\hbar^2}{\pi\,\mu e^2}\,\Gamma_1, \qquad \Gamma_1 = \int_0^{\infty}\widetilde{Z}\,Y^2\big(\widetilde{Z}\big) d\,\widetilde{Z}\,. \tag{41}$$

Table 1 lists Γ, $\overline{F}$.,Γ_1, and ξ_0 at various κ. Using (19), (38), and (41) one can calculate the electron and total energies, as well as the effective electron radius for the tabulated κ.

Figure 2 depicts the dependence of dimensionless total energy $|W|$ on κ. As is seen, there are

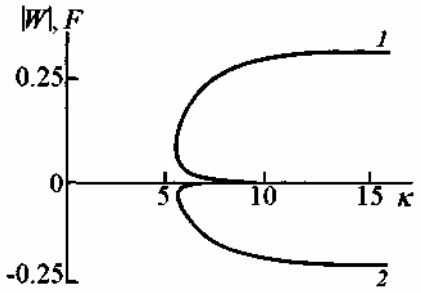

Figure 2. Dependencies of the dimensionless elect-ron $|W|/\left(\pi^2\mu e^4/\widetilde{\varepsilon}^2\hbar^2\right)$ (1) and total $F\left(\pi^2\mu e^4/2\widetilde{\varepsilon}\,\hbar^2\right)$ (2) energies on the parameter $\kappa = \pi e^4\mu R/\widetilde{\varepsilon}\,\hbar^2$.

Table 1. Numerical parameters of the problem.

ξ_0	κ	Γ	F	Γ_1
4.00	16.02	4.005	-1.33	2.773
3.00	12.11	4.039	-1.33	2.774
2.60	10.61	4.084	-1.34	2.779
2.20	9.198	4.181	-1.34	2.795
2.00	8.530	4.265	-1.34	2.814
1.80	7.899	4.388	-1.35	2.846
1.60	7.313	4.571	-1.37	2.903

1.40	6.783	4.845	-1.39	3.000
1.20	6.323	5.269	-1.43	3.168
1.00	5.959	5.959	-1.49	3.465
0.80	5.736	7.170	-1.61	4.020
0.60	5.759	9.598	-1.83	5.182
0.40	6.336	15.84	-2.30	8.253
0.20	9.013	45.07	-3.80	22.82
0.18	9.660	53.67	-4.14	27.11
0.16	10.48	65.49	-4.56	33.02
0.14	11.54	82.46	-5.11	41.50
0.12	12.98	108.1	-5.84	54.33
0.10	15.00	150.0	-6.87	75.25
0.08	18.05	225.6	-8.40	113.1

two solutions at specified κ. The upper branch corresponds to the external states in which the electron localizes mainly outside the cluster, the lower branch does to the internal states localized inside the cluster. The minimum value κ_{rnin} =5.71 corresponds to the bifurcation point where these solutions merge, indicating the minimum cluster size $R_{\min}$ at which the electron is bound to the cluster. According to (36), this size (in angstroms) is equal to

$$R_{\min} = \frac{3,03}{\pi}\,\frac{\widetilde{\varepsilon}\, m_0}{\mu}\ (\text{Å})\ . \tag{42}$$

7. Application of the theory to ammonium clusters

We applied the above results to the clusters consisting of polar molecules of $(NH_3)^-_n$ type. The experimentally found critical number of molecules in these clusters is n_c = 36. For the higher numbers of molecules the electron is bound to the cluster [4] and localized in it with the state energy W=(-1.25+2.63$n^{-1/3}$)eV, while at $n < n_c$ the electron is delocalized.

According to our results, electrons can be captured by the clusters in superstrong magnetic field even at $n<n_c$. To estimate the critical number R when the electron is localized, we use the relationship $R = R_s\, n^{1/3}$, where R_s is the effective radius of ammonium molecule. Using data from [1-3] and (42), we find that n_c = 1 for the clusters in magnetic field. Therefore, the electron states are bound to the cluster in a wide range of the number of cluster molecules from 1 to 36. We estimate the energies of these electron states and the magnetic field required to bind the electron at the ammonium cluster with n = 8. At R_s = 2.85Å [1-3], the cluster size is R = 5.7 Å. Using $\widetilde{\varepsilon}$ =1.92 and $\mu \approx m_0$ [1-3], we find by (38) κ =17.5. According to Table 1, it corresponds to $\Gamma \approx 212$ and 4 for the upper and lower branches of solutions. We calculate $W\sim$ -10^{-3}eV by (19), $F\sim$ -0.5 × 10^{-4} eV by (41) and $r_z \approx$ 70Å by (31) for the upper branch solutions. The field is quantizing for this branch if it exceeds $H \sim 10^5$ Oe.

We also find that $W \approx$ -2.3eV, $F \approx$ –0.7eV, and $r_z \approx$ 1.3 Å for the lower branch. Therefore, it is the small-sized state, and the continual approximation is not valid to describe this state. For this solution the field is quantizing only at superstrong values, $H \sim 10^8$ Oe.

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Appendix[1]
Asymptotic solution to dimensionless equations (17) as $\xi_0 \to 0$.

We denote $\xi_0 = \alpha$ and put

$$\zeta = \frac{\widetilde{Z}}{a}\left(=\frac{Z}{R}\right),\quad Y = \frac{U}{a},\quad U(\zeta) = a\,Y(a\,\zeta). \tag{A1}$$

Then, we have the equation for

$$U''(\zeta)+U(\zeta)\left[U^2(\zeta)-U^2(1)\right]-a^2U(\zeta)=0\,,\quad |\zeta|\le 1\,, \tag{A2}$$

subject to the boundary conditions

$$U'(1)=-aU(1)\,,\quad U'(-1)=aU(-1)\,.$$

As $\alpha \to 0$, the nonzero solution to the boundary problem (A2) is assumed to tend to solution of the limiting problem corresponding to $a = 0$. The limiting problem is degenerated, i.e., any $U(\zeta) \equiv C$ is the solution to (A2). But this degeneracy disappears at $\alpha > 0$. We put

$$U(\zeta)=C+aV(\zeta)+O\left(a^2\right), \tag{A3}$$

where C ≠ 0 is a nonzero unknown constant. Substituting (A3) into (A2), we find

$$V''(\zeta)+2C^2\left[V(\zeta)-V(1)\right]=0\,, \tag{A4a}$$

$$V'(1)=-C\,,\quad V'(-1)=C\,, \tag{A4b}$$

whence

$$V(\zeta)=A\cos(\mu\zeta)+V(1)\,,\quad \mu^2=2C^2. \tag{A5}$$

Substituting ζ = 1 into (A5), we have cosμ = 0. If μ = 1/2π, then $C = \pi/2\sqrt{2}$ and boundary conditions (A4b) are fulfilled at $A = 1/\sqrt{2}$. The value *V(I)* is as usual not determined in this approximation. Taking into account the terms $O(a^2)$, we find V(1) = 0.
Hence, at small α

$$U(\zeta)\approx\frac{\pi}{2\sqrt{2}}+\frac{a}{\sqrt{2}}\cos\left(\frac{\pi}{2}\zeta\right). \tag{A6}$$

The calculated solutions to (A2) at $\alpha \le 0.5$ differ from (A6) less than by 2%.
We note that expressions (A3) and (A5) yield not only an approximation for $U = U(\zeta, a)$. According these formulas, the solution to (A2) is unambiguous at small a, each root of cos μ = 0 corresponds to a branch of the solution (existing probably only in a narrow interval of a). The larger *C* correspond to smaller |*W*| (see (19) and (26)).

At fixed *a* each solution to (A2) corresponds to *a* solution of original problem (13), but different solutions have distinct *R*. We note that $\alpha \to 0$ corresponds to $R \to \infty$ according to (27). One can find the solution to (13) to be not unique at fixed (large) *R*. The additional solutions to (13) and a prove of possible expansion (A3) will be reported elsewhere.

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