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Binding of D^- Ions in a Magnetic Field

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I present the first strong evidence for the observation of D^- centers in a semiconductor with a simple conduction band minimum at $k=0$. The identification is based primarily upon agreement between the predicted and observed curve of photodetachment threshold frequency vs magnetic field in CdS. New, relatively simple and physically motivated variation trail functions are employed which give eigenvalues of sufficient accuracy for critical comparison with experiment.

When a dilute assembly of shallow donors in an uncompensated semiconductor is subjected to room-temperature radiation some of the electrons initially excited into the conduction band by photoionization of donors may, at low temperatures, recombine with neutral donors to produce isolated D^- centers. Such centers consist of a hydrogenic donor with an extra electron attached; they have been found in Si and Ge,[1-5] semiconductors with multiple conduction-band minima. Surprisingly, no well-substantiated observations of D^- ions in any of the many semiconductors with "simple" conduction bands having a single isotropic $k=0$ minimum have been reported. D^- ions in such semiconductors would be analogs of H$^-$ ions in the same way that simple hydrogenic donors are analogous to hydrogen atoms. The H$^-$ ion has, in theory, a rich magnetic structure at fields much higher than can be reached in the laboratory.[6-9] This structure could, however, be elucidated at laboratory field strengths by experiments on D^- ions associated with "simple" conduction bands.

In this paper, I show by physical arguments how relatively simple variational trial functions for H$^-$ states can be constructed which turn out to give accurate level energies in the field range of interest. My results are used to interpret previously published low-temperature magnetoabsorption data[10] on CdS, and a case is made for identifying one of the lines seen in that material as photodetachment of an electron from the ground state of the D^- ion.

The H$^-$-ion zero magnetic field has exactly one bound state,[11] a singlet S level, which has been intensively studied theoretically.[12] The binding energy of this level is ~ -0.0555.[13] (By "binding energy" I shall always mean the minimum energy required to remove a single electron from the H$^-$ or D^- ion without changing the two-electron spin configuration.)

For arbitrarily small nonzero magnetic field, there are, as shown in Ref. 8, an infinite number of bound states of H$^-$, at least one such state for each M_L for $M_L = 0, -1, -2, \ldots$, where M_L is the projection of the total electronic orbital angular momentum (in units of $\hbar$) of the H$^-$ ion on the magnetic field direction. Although the trial functions employed in the discussion in Ref. 8 are not capable of giving accurate binding energies[14] they suggest that, consistent with the results presented here, the binding decreases monotonically with increasing $|M_L|$ for fixed small magnetic field. In this paper the main calculational effort is devoted to finding accurate binding energies for the lowest states with $M_L = 0$ and -1.

(A) *Ground singlet state* ($M_L = 0$).—The Hamiltonian, H_{total}, for H$^-$ in a uniform magnetic field $\vec{B}$ along the z direction can be written[13]

$$H_{\text{total}} = H(1) + H(2) + \frac{2}{r_{12}} + \gamma M_L + g^* \gamma_s M_s ,$$
$$H(i) = \nabla_i^2 - \frac{2}{r_i} + \frac{\gamma}{4}\rho_i^2 \quad (i = 1, 2), \tag{1}$$

where $\rho_i^2 = x_i^2 + y_i^2$, M_s is the total projection of the spin angular momentum along z, and γ and γ_s are the dimensionless magnetic fields $\hbar\omega_c/2R$ and $\beta B/R$, respectively, with ω_c the electron cyclotron frequency and β the Bohr magneton. (In semiconductors as a rule $\gamma > \gamma_s$ and $g^* \neq 2$.) Noticing that the diamagnetic term $\gamma^2\rho^2/4$ is just a two-dimensional harmonic-oscillator potential I can expect that its effect on the wave function of the one H$^-$ level bound at zero field could be well described as a combination of a spherically symmetric compression and an elongation along z. These two effects can be conveniently represented by taking as a trial function

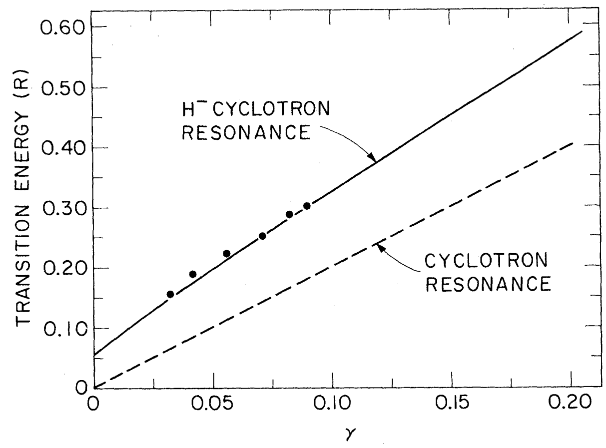

FIG. 1. The solid curve shows the calculated minimum energy required to excite an electron from the D^- singlet ground state to the first excited Landau level vs the dimensionless magnetic field, γ. The free-electron cyclotron energy is plotted as the dashed curve. Dots are experimental points from Ref. 10.

$$\psi_0(\gamma) = [1 + \alpha(Z_1^2 + Z_2^2) + \epsilon(Z_1^4 + Z_2^4)] \exp[-\delta(r_1^2 + r_2^2)]\psi_0(\gamma = 0), \tag{2}$$

where α, ϵ, and δ are variational parameters. Depending upon how much accuracy at very low fields is required one can choose for $\psi_0(0)$ any of the many zero-field H$^-$ wave functions in the literature.[12] I have in fact used one of the simplest of these, the Chandrasekhar wave function ψ_{Ch}, described in Ref. 12, in the calculations taking

$$\psi_0(\gamma = 0) = \psi_{\text{Ch}} = (1 + c|\vec{r}_1 - \vec{r}_2|)[\exp(-K_1 r_1 - K_2 r_2) + \exp(-K_2 r_1 - K_1 r_2)]; \tag{3}$$

here c, K_1, and K_2 are variational parameters.

At zero field, the trial function underestimates the binding energy by $\sim 0.0036R$ and I anticipate that, at least for $\gamma \lesssim 0.5$, the error is not significantly greater than that. Detailed discussion of the accuracy of binding energies obtained by minimizing $\langle\psi_0(\gamma)|H_{\text{total}}|\psi_0(\gamma)\rangle / \langle\psi_0(\gamma)|\psi_0(\gamma)\rangle \equiv E_0(\gamma)$ with respect to all of the variational parameters will be given elsewhere.

Binding energies relative to the bottom of the first excited Landau-level band are obtained by subtracting $E_0(\gamma) - 2\gamma$ from the energy of the H atom[15, 16] at magnetic field γ and are plotted as the solid curve in Fig. 1, labeled "H$^-$ cyclotron resonance."

(B) *Excited states*, $|M_L| > 0$.—For describing states at low fields which are unbound at zero magnetic field an entirely different approach is required. In this case, the outer electron, being only weakly bound, will travel in a large cyclotron orbit centered on the inner atom, spending most of its time at large distances from the H atom. The central binding force on the outer electron will arise primarily from the dipole field of the H atom, which is polarized by the Coulomb field of the distant electron. The ground-state wave function for an H atom polarized by an electron fixed at a large distance r_1 from the center of the atom can be obtained in the form[17]

$$[1 - (r_2^2/2 + r_2)\cos\theta_{12}/r_1^2] \exp(-r_2), \tag{4}$$

where $\vec{r}_2$ is the displacement of the H atom electron and $\cos\theta_{12} = \vec{r}_1 \cdot \vec{r}_2 / r_1 r_2$. Motivated by (4), I describe the inner atom in the trial function by

$$\chi(r_1, r_2) = [1 - c(r_2^2/2 + r_2)\cos\theta_{12}/(r_1^2 + b)] \exp(-\xi r_2^2 - K_2 r_2), \tag{5}$$

where the variational parameter c controls the strength of the polarization, b cuts off the polarization at small separations, r_1, and $\exp(-\zeta r_2^2)$ accounts for compression of the H atom by the magnetic field. To complete the trial function I first multiply $\chi(r_1,r_2)$ by an orbital wave function for the outer electron, which I choose in the form

$$\Phi_{|M_L|}(r_1) = \exp(iM_L\varphi_1)\rho_1^{|M_L|}\exp(-\rho_1^2/A^2)\exp(-K_1 r_1). \tag{6}$$

The trial function now becomes (ignoring spin)

$$\psi_{|M_L|}(r_1,r_2) = \Phi_{|M_L|}(r_1)\chi(r_1,r_2).$$

Binding energies plotted in Fig. 2 for $M_L = -1$, -2, and -4 are estimated from the normalized form of $\psi_{|M_L|}$ by varying, in the appropriate energy expectation value, all parameters except ζ and K_2. Those two parameters are determined beforehand by minimizing the H-atom energy using $H(2)$ given by (1) and the trial function $\exp(-\zeta \times r_2^2 - K_2 r_2)$. (At the larger values of γ, the H-atom energy so obtained, E_{H}, begins to deviate significantly from the "exact" energies of Refs. 15 and 16. This deviation is plotted as a dashed line in Fig. 2.) The estimated binding energies in Fig. 2 are calculated by subtracting from E_{H} the lowest H^- energy obtained. Estimated binding energies less than $\sim 10^{-5}$ could not be distinguished from zero.

For the $M_L = -1$ level, I have studied singlet and triplet binding energies using the symmetrized functions $\psi_1(r_1,r_2) \pm \psi_1(r_2,r_1)$ (minus sign for triplet). From Fig. 2 it is clear that exchange strongly enhances binding at the higher fields for $M_L = -1$. In fact, considerably stronger binding is found here than in the best previous calculations,[6] which employed large determinants of Slater orbitals. The triplet wave functions at low γ are markedly elongated along the magnetic field and, in semiconductors, the triplet D^- ions most probably form a D^- band. [A useful but rather crude estimate of the parameter K_1 in (5) is $K_1 \cong (\text{binding energy})^{1/2}$, whereas $A^2 \cong 4/\gamma$.]

Remarkably, *no* bound *singlet* states were found for $M_L = -1$ over the field range $0 \leq \gamma \leq 0.3$. This suggests that there may be an effective repulsive barrier between the H atom and free electrons in the spin singlet state. [Also, for $\gamma \leq 0.3$, no triplet bound state is found for antisymmetrized $M_L = 0$ wave functions constructed from $\psi_0(r_1,r_2)$.]

I propose that the higher-frequency line reported in the low-temperature infrared magnetoabsorption experiment in CdS (Ref. 10) is an M_s-conserving transition of the form

$$D^-(\text{singlet ground state}) \rightarrow D(\text{ground state}) + e^-(\text{excited Landau level}),$$

where the wave function for the free electron is

$$e^{i\varphi}\rho\exp(-\gamma\rho^2/4)\exp(\pm ik_z z), \tag{7}$$

at large distances along z from the H atom. Since this is a photodetachment process the transition energy to be compared to the theoretical binding energy is not the energy at the peak as plotted in Ref. 10 but rather the low-energy threshold of the absorption. From the line shape given in Ref. 10 for 6.65 T, I estimate that the threshold is 6.3 cm^{-1} below the peak. Assuming that this difference remains constant for all peaks and making the appropriate correction I place the experimental points on Fig. 1 as shown by the dots. These are no adjustable parameters employed; I used an averaged effective mass[18] $m_{\mathrm{CdS}}/m = 0.166$ and a value[19] $R = 261\ \mathrm{cm}^{-1}$, giving $\gamma = 1$ at 93.5 T. The agreement appears satisfactory.

If the final state of the detached electron were exactly given by (7), it would be hard to understand why the line peak should be so far removed from the threshold since the density of final states

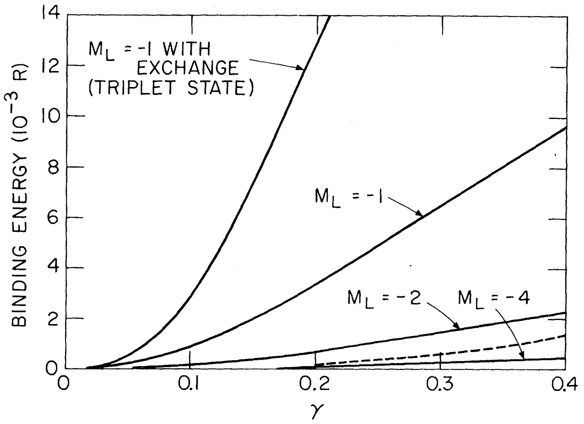

FIG. 2. Estimated binding energy vs dimensionless magnetic field γ is plotted for various trial functions (solid curves). These curves are labeled by values of angular momentum quantum number M_L. Only the $M_L = -1$ curve "with exchange" is calculated with an antisymmetrized wave function. The dashed curve is described in the text.

at threshold diverges in a magnetic field. However, if, as suggested above, the ejected electron feels a repulsive potential then the transition matrix element would become small at low kz, thereby providing a mechanism for shifting the photodetachment peak to significantly higher energy than the threshold.

Because the overlap of the wave function in (7) and the H atom decreases as $\gamma \to 0$, I expect that the transition probability to the Landau level of interest should decrease with magnetic field (a simple calculation shows that the square of the transition matrix element vanishes like γ^2 as $\gamma \to 0$). Thus my proposed model can account at least qualitatively for the rapid diminution of absorption intensity with decreasing fields reported in Ref. 10.

At the low temperature (1.4°K) and high fields employed in Ref. 10, both the singlet D^- state binding energy and the energy required to flip the spin of a free electron are large compared to k_BT; for example, at $\gamma = 0.05$ ($B \cong 4.7$ T) the binding energy of the D^- ground state is ~ 37°K and the spin-flip energy is 5.7°K (the triplet $M_L = -1$ binding energy, as calculated here, is only 0.2°K).[20] I must conclude from these numbers that if the singlet D^- is formed from a population of spin-equilibrated free electrons interacting with spin-equilibrated neutral donors, the lifetime of the D^- must be large enough to establish something approaching thermal equilibrium between the D^- centers and the steady-state population of conduction electrons. In this picture, free electrons with minority-spin orientation are constantly being removed by trapping on neutral donors, and neutral donors with a minority-spin electron are constantly being converted to D^- centers. With sufficiently long D^- lifetime this would permit a sizable singlet D^- population to build up even at large fields and low temperatures.

It is tempting to speculate that a second, lower-energy line also reported in Ref. 10 might arise from a bound triplet D^- state. Although the calculations presented here give binding energies for triplet states which seem too small to account for the second line reported in Ref. 10, my study has not exhausted all possibilities for D^- excited states which are relatively deeply bound at small γ. Further work is in progress.

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