

## The hydrogen atom in intense magnetic fields: Excitons in two and three dimensions

H. Lehmann and N.H. March  
University of Oxford  
Dept. Theoretical Chemistry  
5 South Parks Road  
Oxford OX1 3 UB  
United Kingdom

### Abstract

As a model of excitonic behaviour the paper concerns itself with the one-electron states generated by a bare Coulomb potential  $-Ze^2/r$ , plus an applied magnetic field  $H$  which is assumed intense. A quantity which reflects the entire one-electron level spectrum  $\epsilon_i$  and the corresponding wave functions  $\psi_i$  is the canonical density matrix  $C(\vec{r}, \vec{r}', \beta) = \sum_i \psi_i(\vec{r}) \psi_i(\vec{r}') \exp(-\beta \epsilon_i)$  whose trace is the partition function  $Z(\beta)$ . The inverse Laplace transform of  $C/\beta$  yields the Dirac density matrix  $\rho(\vec{r}, \vec{r}', E)$ , its diagonal element being the integrated local density of states. For free electrons in an intense field  $\rho_0(\vec{r}, E) = H(E - H)^{1/2}$  in three dimensions and in the presence of the Coulomb potential the Thomas-Fermi approximation replaces  $E$  by  $(E + Ze^2/r)$ . One can approximate, albeit somewhat crudely, the lowest energy state by finding the energy,  $E_l$  say, such that  $\int_{-\infty}^{E_l} \rho_{TF}(E) = 2$ . Such a procedure leads to a large error in  $E_l$  for  $H = 0$  but is expected to be a better approximation in a large field.

Applying the same approximation in two dimensions, with the magnetic field perpendicular to the plane of confinement assumed for the electrons, leads again to an estimate for the lowest one-electron state in an intense field. This motivates then a further study of this two-dimensional case, in which the pure cylindrical symmetry of the two-dimensional zero field case is preserved.

Finally, in an Appendix, the bare Coulomb limit of a recent, self-consistent field, treatment by Lieb et al. of atoms in a 'hyperstrong field' such that, in suitable units,  $H \gg Z^2$  is set out.

## 1. Introduction

The Hamiltonian for a hydrogen atom in a magnetic field  $H$  along the  $z$ -axis is in atomic units for a nuclear charge  $Z$ :

$$\hat{H} = -\frac{\Delta}{2} - \frac{Z}{r} - \frac{iH}{2} \frac{\partial}{\partial \phi} + \frac{1}{8} H^2 r^2 \sin^2 \vartheta \quad (1)$$

in spherical polar coordinates. For small fields  $H$  the linear term is dominant which commutes with the zero field Hamiltonian. In quantum mechanics a this limit consequently yields a level shift only depending on the magnetic quantum number  $m$  and leaves the hydrogen eigenfunctions unaltered. In the strong field limit the last term in Hamiltonian (1) dominates, giving a parabolic confinement in the  $x - y$  plane. This, of course, is known since Landau's original treatment of charges in a magnetic field, i.e. referring the wave equation to a modified harmonic oscillator. The magnetic field, hence, changes the symmetry of the system from an unperurbed hydrogen atom to a cylindrically quenched atom around the  $z$ -axis.

Further insight in the symmetry of the problem can be gained by studying the classical Lagrangian:

$$L = T - V = \frac{1}{2} \left[ \dot{r}^2 + r^2 \dot{\vartheta}^2 + r^2 \sin^2 \vartheta (\dot{\phi} + H)^2 \right] + \frac{Z}{r} \quad (2)$$

Introducing via a Legendre transform the generalized momenta

$$p_r = \dot{r} \quad , p_\vartheta = r^2 \dot{\vartheta} \quad , p_\phi = r^2 \sin^2 \vartheta (\dot{\phi} + H) \quad (3)$$

it is immediately seen that the resulting Hamiltonian is form-invariant to that of the bare Keplerproblem:

$$\hat{H} = \sum p_i \dot{q}_i - L = \frac{1}{2} \left[ p_r^2 + \frac{1}{r^2} p_\vartheta^2 + \frac{1}{r^2 \sin^2 \vartheta} p_\phi^2 \right] - \frac{Z}{r} \quad (4)$$

The physical difference is condensed in the redefinition of the momentum in  $\phi$ -dimension. Since integrals of motion can be described by vanishing Poisson brackets it is clear that any constant of motion in the Kepler problem has an

analogue (if appropriately redefined quantities are used) in the magnetic field case. In this sense the atoms with and without external magnetic field have the same symmetry and the 'quenched' atom is in essence still a spherical one. It will be seen below that this fact expresses itself in the quantal case in certain scaling properties. Semiclassically, this argument justifies the use of the spherically symmetric Thomas-Fermi theory. Introducing, as in some quantum dot models, an additional confining potential - usually parabolic - destroys the this symmetry. This model may, however, be useful in establishing the effects of the magnetic field other than the mere confinement. This discussion is carried out below using an exact result for the two-dimensional canonical density matrix for a localized Wigner oscillator.

## 2. Semiclassical theory of the lowest level of the hydrogen atom in an intense magnetic field

For  $N/2$  occupied one-electron levels of Hamiltonian (1) in the intense field limit, March and Tomishima [1] show by means of the Thomas-Fermi (TF) semiclassical approximation that the total energy  $E_{TF}^{Coul}$  scales according to

$$E_{TF}^{Coul} = const. Z^{9/5} H^{2/5} (N/Z)^{3/5} \quad (5)$$

It must be stressed that eqn. (5) is valid only at high fields - the zero field result

$$E_{TF}(H = 0) = const. Z^2 N^{1/3} \quad (6)$$

cannot be regained.

To address the question as to the scaling of the lowest energy level  $E_l$  let us form the chemical potential  $\mu$  from eqn. (5). This can be done using the 'thermodynamic' result

$$\mu = \left. \frac{\partial E}{\partial N} \right|_Z \quad (7)$$

which goes back to Hulthen. Substituting eqn. (5) into eqn. (7) yields

$$\mu_{TF}^{Coul} = const. Z^{6/5} H^{2/5} N^{-2/3} \quad (8)$$

But if we put  $N = 2$  in eqn. (8), we obtain immediately the scaling of the lowest energy level,  $E_l$ , as

$$E_l = const. Z^{6/5} H^{2/5} \quad (9)$$

This then is the modification of the  $1s$  level,  $E_{100}$  of the hydrogen-like atom with nuclear charge  $Ze$ , namely  $E_{100} = -\frac{(Ze)^2}{2a_0}$  with  $a_0$  the Bohr radius, in the case of the intense magnetic field limit. Of course, for the future, it will be of considerable importance to develop a fully quantal treatment which will interpolate smoothly between  $E_{100}$  and the level  $E_l$  of eqn. (9). One must caution that it cannot be expected that the semiclassical theory used in deriving the scaling in eqn. (9) could yield a precise value for the constant there.

To gain a little further insight into the origin of the scaling (9) in the high field regime, let us introduce a classical magnetic radius  $l_c$ :

$$l_c = H^{-1/2} \quad (10)$$

Rewriting eqn. (9) then yields

$$E_l = const. \left( \frac{Z}{l_c} \right) \left( \frac{Z l_c}{a_0} \right)^{1/5} \quad (11)$$

The characteristic energy in eqn. (11) has evidently been chosen as  $(Ze^2/l_c)$ , the second term then describes the transition from a magnetic to an atomic scale by the ration of typical lengths to the power  $1/5$ .

To date it has not proved possible to make a fully quantal analytical theory of  $E_l$  even in the intense field limit. However, we show below that the problem simplifies considerably if we confine electronic motion, still in the potential  $-Ze^2/r$  to a plane perpendicular to the magnetic field  $H$ . In view of the symmetry discussion in the introduction this step preserves the 'spherical' symmetry of the two-dimensional hydrogen atom.

## 3. Two-dimensional motion

### 3.1 Modification of semiclassical TF-theory to two dimensions

Before embarking on a fully quantal treatment, let us briefly summarize the way in which the the TF argument of the previous section is affected by the dimensionality change.

### Zero-field case

To illustrate the 2D procedure in an example where the exact solution is already known, let us begin with zero magnetic field. Then the (constant) chemical potential  $\mu$  is made up of two parts, kinetic and potential, both of which vary with position  $r$ :

$$\mu = \frac{1}{2m} p_f^2(r) - \frac{Ze^2}{r} \quad (12)$$

where  $p_f(r)$  denotes the maximum, or Fermi, momentum at  $r$ . By phase space arguments, with cells of area  $h^2$  holding two electrons, one has the electron density  $\rho(r, \mu)$  equal to

$$\rho(r, \mu) = \frac{2\pi}{h^2} p_f^2(r) \quad (13)$$

Inserting eqn. (12) into (13) and letting  $\mu \rightarrow E$  we can calculate the ground-state energy  $E_l$  again by writing

$$2 = \int_0^{r_c} 2\pi r \rho(r, E) dr \quad (14)$$

where  $r_c$  is the classical radius defined by

$$E + \frac{Ze^2}{r_c} = 0 \quad (15)$$

Using eqns. (12) to (15), one readily finds (going over to atomic units):

$$E_l^{TF} = -\frac{Z^2}{2} \quad (16)$$

While eqn. (16) has the correct scaling with  $Z$ , the exact result [2] is:

$$E_l = -2Z^2 \quad (17)$$

### High magnetic field ground state

Using the work of Sondheimer and Wilson [3] the free electron result implicit in eqns. (12),(13) generalizes in the high field limit in two dimensions to

$$\rho_0^{(2D)}(E, H) = \begin{cases} H/2 & \text{if } E \geq H/2 \\ 0 & \text{if } E < H/2 \end{cases} \quad (18)$$

In three dimensions the result is, as mentioned above

$$\rho_0^{(3D)}(E, H) = \begin{cases} \frac{H}{2}(E-H)^{1/2} & \text{if } E \geq H/2 \\ 0 & \text{if } E < H/2 \end{cases} \quad (19)$$

Proceeding as above, i.e. replacing  $E$  by  $E + Ze^2/r$  and defining an appropriate  $r_c$  gives for the ground state energy in two dimensions:

$$E_l = -H^{1/2}Z + H/2 \quad (20)$$

Noting that the dimension of the energy in atomic units is  $(length)^{-2}$ , the first term in (20) presents a geometrical mean between an atomic and a magnetic energy. The second term is merely the shift introduced in eqn. (18). Its physical origin is the field energy stored in the system.

## 3.2 Partition function and generalized probability current

The canonical density matrix  $C$  as introduced above is a solution of the Bloch equation

$$\hat{H}_r C(\vec{r}, \vec{r}', \beta) = -\frac{\partial}{\partial \beta} C(\vec{r}, \vec{r}', \beta) \quad (21)$$

where the Hamiltonian we are interested in was given in (1). Separating the Sondheimer-Wilson result from the overall  $C$ :

$$C = C_{SW} C^* \quad (22)$$

yields an equation for  $C$  which becomes particularly simple on the diagonal:

$$\left[ -\frac{\Delta}{2} - 2iH \frac{\partial}{\partial \phi} - \frac{Z}{r} \right] C^*|_{r=r'} = -\frac{\partial}{\partial \beta} C^*|_{r=r'} \quad (23)$$

The second term in the Hamiltonian in eq. (23) is the  $z$ -component of the angular momentum which commutes with the hydrogen Hamiltonian. Therefore  $C^*$  can be characterized by known quantities for the hydrogen atom. It should be mentioned that this property is used in quantum mechanics as an approximate, low-field treatment for the Zeeman effect, disregarding the  $H^2$ -term in the Hamiltonian (1). Since, however, this term was treated accurately in the separation (22), the following scaling relations are exact.

Using the wave function representation of  $C$  (see above) and recognizing that the angular momentum term in eqn. (23) gives rise to an energy shift dependent on the magnetic quantum number only,  $C^*$  can be referred to the known result  $C_Z$  [4]:

$$C^*(r\vartheta\phi r'\vartheta'\phi') = C_Z(r\vartheta\bar{\phi}r'\vartheta'\bar{\phi}') \quad (24)$$

where

$$\bar{\phi} = \phi - iH\beta \quad , \quad \bar{\phi}' = \phi' + iH\beta \quad (25)$$

It must be stressed again that  $C^*$  has to be taken on the diagonal. The scaling (24) therefore relates the diagonal element of  $C^*$  to the off-diagonal element of a complex angle variable in  $C_Z$ . Due to the high symmetry of the hydrogen atom  $C_Z$  can be given in only two variables [4]:

$$C_Z = C_Z(x, y) \quad (26)$$

where

$$x = r + r' + r_{12} \quad \text{and} \quad y = r + r' - r_{12} \quad (27)$$

The scaling (25) obviously only affects the inter-particle distance  $r_{12}$  which becomes purely imaginary on the diagonal:

$$\bar{r}_{12}^2 = 2r^2 \sin^2\vartheta [1 - \cosh 2H\beta] \quad (28)$$

So far the analysis has been three-dimensional. From (28) it can be seen that the two-dimensional case just picks out the plane with maximal effect of the magnetic field  $H$ ; no symmetry is changed. This is in accordance with the classical arguments of the introduction. At this stage it is important to note that an exact result for the Slater sum  $S$  (which is the diagonal element of the canonical density matrix) has been obtained:

$$S = S_{SW} C_Z(2r + \bar{r}_{12}, 2r - \bar{r}_{12}) \quad (29)$$

where

$$S_{SW} = (2\pi\beta)^{-3/2} \frac{H\beta}{2} \left[ \sinh \frac{H\beta}{2} \right]^{-1} \quad (30)$$

Note that the result (29) is not restricted to the high field limit. Also,  $S = S(r, \vartheta)$  from eqn. (29), in contrast to  $S_Z = S_Z(r)$ . It seems remarkable that the additional variable does not destroy the scaling.

Further physical insight can be obtained by studying the probability current as defined in [5];

$$\vec{J}(\vec{r}, \beta) = -\frac{i}{2}(\nabla - \nabla')C(\vec{r}\vec{r}', \beta)|_{r=r'} - \vec{H} \times \vec{r}C(\vec{r}\vec{r}', \beta) \quad (31)$$

Whereas the usual wave function current expresses the conservation of the norm, the  $\vec{J}$  of eqn. (31) corresponds to the conservation of the density matrix. The second term in (31) stems from the rotation of the free electrons in the magnetic field, this feature being described in the Sondheimer-Wilson result. The physically interesting variable for the presence of a nucleus therefore is:

$$\vec{J}^* = -\frac{i}{2}(\nabla - \nabla')C^*|_{r=r'} \quad (32)$$

Using the derived scaling one eventually finds:

$$\vec{J}^* = \vec{e}_\phi \frac{1}{\sqrt{2}} \sinh 2H\beta [\cosh 2H\beta - 1]^{-1/2} \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) C_Z(x = 2r + \bar{r}_{12}, y = 2r - \bar{r}_{12}) \quad (33)$$

From the expression given in [4] one convinces oneself easily that the current  $\vec{J}^*$  is a purely real quantity. The result (33) correctly contains the vanishing of the current for zero field; for high fields the current increases exponentially with the Larmor frequency.

### 3.3 Some comments on the confinements of quantum dots

To conclude this paragraph another interesting limiting case can be discussed. March and Tosi [6] gave an exact result for the two-dimensional canonical density matrix for an electron in a magnetic field with parabolic confinement. This additional confinement is often used to model quantum dots as, e.g., discussed by Halonen et al. [7]. The absence of the Coulomb interaction in the result of March and Tosi points not only to the limit of dominant field strengths but possibly to materials with very high dielectric constants. We give here again the diagonal element, i.e. the Slater sum:

$$S_{MT}(r, \beta) = f(\beta) \exp[-4r^2 h(\beta)] \quad (34)$$

with

$$h(\beta) = \frac{b}{4} \left[ \coth \frac{bH\beta}{2} - \cosh \frac{H\beta}{2} / \sinh \frac{bH\beta}{2} \right] \quad , \quad (35)$$

$$f(\beta) = \frac{bH}{4\pi} \left[ \sinh \frac{bH\beta}{2} \right]^{-1} \quad \text{and} \quad (36)$$

$$b = \sqrt{1 + \frac{4k}{H^2}} \quad (37)$$

where  $k$  is the force constant of the confinement. Note, that in (34) the translational invariance of the electron gas is broken by the confinement, hence the  $r$ -dependence. In the limit of high fields with simultaneous control of the confinement it can be shown that

$$h(\beta) \rightarrow \frac{k\beta}{8} \quad (38)$$

and

$$f(\beta) \rightarrow \frac{\exp(-\frac{H\beta}{2})}{4\pi} \left[ H - k\beta + \frac{2k}{H} \right] \quad (39)$$

While the spatial dependence in this regime is governed by the confinement, in the function  $f$  competition between magnetic field, confinement and ideal gas behaviour can be seen.

## Summary

Under the assumption that much of the rich behaviour of excitons in semiconductors can be understood by modelling them as effective hydrogen atoms a variety of results has been discussed. Symmetry properties lead to an exact scaling for the Slater sum of an electron in the superposition of Coulomb potential and external field. Semiclassical Thomas-Fermi theory can be employed to derive a scaling relation for the lowest lying state. The applicability of a spherically symmetric semiclassical theory can be justified by basic symmetry observations. Contact with recent work on quantum dot models in the limit of negligible Coulomb interaction has been established. It has been our intention to break up the mathematical richness of the problem into simpler limiting cases which can be taken as starting points. For the high field limit a semiclassical theory should provide insight into the dominant effects. Furthermore, the exact result given for the Slater sum provides a starting point for thermodynamics since the Helmholtz Free Energy is easily computed as the logarithm of its all-space integral.

## Appendix A

### High field regime such that $H \gg Z^3$

We shall attempt, in this Appendix, to extract from the work of Lieb et al. [8] the Coulomb limit, of interest in the present context, in their regime 5 i.e.

$$H \gg Z^3 \quad (40)$$

in suitable units (different from those in the main text).

To do so, we write their self-consistent field ground-state energy in the form

$$E_{scf} = Z^3 [\ln \eta]^2 E^{intensefield}(N/Z) \quad (41)$$

where  $\eta = H/Z^3 \gg 1$  while

$$E^{intensefield} = -\frac{\lambda}{4} + \frac{\lambda^2}{8} - \frac{\lambda^3}{48} \quad ; \quad \lambda \leq 2 \quad (42)$$

As in the zero field bare Coulomb case, we assume we can extract the Coulomb limit by letting  $\lambda \rightarrow 0$  to find

$$E^{Coulomb} = -\frac{Z^3}{4} [\ln \eta]^2 (N/Z) \quad (43)$$

This result is remarkable in that it is proportional to the number of electrons  $N$ , and if we define the chemical potential  $\mu^{Coulomb} = \partial E^{Coulomb} / \partial N$  we have

$$\mu^{Coulomb} = \frac{E^{Coulomb}}{N} = -\frac{Z^2}{4} [\ln \eta]^2 \quad . \quad (44)$$

This would appear to imply therefore, that in the range of validity of the Lieb et al. treatment, the lowest Coulomb energy level is highly degenerate and is given by the above equation.

## References

- [1] N.H.March, Y. Tomishima, *Phys. Rev. D*19, 449 (1979)
- [2] B. Zaslow, M.E. Zandler, *Am. J. Phys.* 35, 1118 (1967)
- [3] E.H. Sondheimer, A.H. Wilson, *Proc. Roy. Soc. Sect. A (London)* 210, 173 (1951)
- [4] S.M. Blinder, *Phys Rev. A*43, 13 (1991), also *Int. J. Quant Chem. Symp.* 18, 293 (1984)
- [5] C. Amivili, N.H. March, *Phys. Rev. A*43, 2528 (1991)
- [6] N.H. March, M.P. Tosi, *J. Phys. A*18, L643 (1985)
- [7] V. Halonen et al., *Phys. Rev. B*45, 5980 (1992)
- [8] E. Lieb et al., *Phys. Rev. Lett.* 69, 749 (1992)