LETTER TO THE EDITOR

Hydrogen molecules in two dimensions

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Abstract. Using a variational method, we have obtained the binding energy and equilibrium distance of a two-dimensional hydrogen molecule (HM), these being much larger and shorter than those of a three-dimensional HM. It is shown that the dimensionality effect on exciton molecules is as important as that of the electron-to-hole ratio of effective masses.

At low temperatures, free electrons and holes, regardless of how they are created in a bulk semiconductor, are bound into excitons by Coulomb forces. By analogy with polyelectronic complexes as first considered by Wheeler (1946), Lampert (1958) and Moskalenko (1958) suggested independently that in a non-equilibrium electron–hole system in a bulk semiconductor, free multiparticle complexes more complicated than the exciton, namely, neutral excitonic molecules (EMs) (bound states of two excitons, often called biexcitons), excitonic ions (bound states of an exciton with an electron or a hole), etc can exist. Since the first work, many attempts have been made to discover these free multiparticle complexes, in particular the EMs, by spectroscopic means. The EM stability was confirmed by reliable variation calculations of Akimoto and Hanamura (1972a, b) and Brinkman *et al* (1973). It is interesting to point out that when the electron and hole effective masses do not differ considerably, the widely used (particularly in molecular spectroscopy) adiabatic approximation is, in general, inapplicable for the four-body problem. The binding energies (in exciton Rydberg units) and the mean inter-hole distances (in exciton Bohr-radius units) of EMs are strongly dependent on the electron-to-hole ratio, σ, of effective masses. In the limits $\sigma = 1$ and 0, the problem of EM stability is, respectively, identical to the problem for the positronium molecule (PM) which was first solved by Hylleraas and Ore (1947) and that for the hydrogen molecule (HM). Therefore, the binding energies and the mean inter-hole distances of EMs (in exciton Rydberg and Bohr-radius units) change monotonically from 0.35 and 1.4 of the HM to 0.027 and 3.47 of the PM as σ increases from zero to one. This is because of the increase of the kinetic energy (in exciton Rydberg units) of the holes with increasing σ.

During the last decade there has been increasing interest in exciton and related optical properties in semiconductor quantum wells (QWs) for their wide applicability to various optielectronic devices. In the optical properties of QWs, excitons play an important role and can yield strong peaks in the spectra even at room temperature and under a relatively strong electric field applied perpendicular to the QW layer.

However, exciton envelope functions can overlap as excitons are created at high density in semiconductor QWs. This gives rise to various non-linear effects: collisions, formation of electron–hole plasmas or creation of EMs. Although the stability, the binding energies and the mean inter-hole distances of EMs in bulk semiconductors have been studied by a number of authors since 1958, the binding energies and the mean distances in corresponding QWs have not been reported to date. It is worthwhile to know the EM differences between QWs and bulk semiconductors. In order to show the dimensionality effect on EMs, we report for the first time the ground-state energy, the binding energy and the equilibrium distance of a two-dimensional (2D) HM in this letter. This is the limiting case of EMs with $\sigma = 0$ in a QW of zero well width with infinite barrier height.

The Hamiltonian for a 2DHM in atomic units can be expressed as

$$H = -\Delta_1 - \Delta_2 - 2/\rho_{a1} - 2/\rho_{b1} - 2/\rho_{a2} - 2/\rho_{b2} + 2/\rho_{12} + 2/R \qquad (1)$$

where Δ_1 and Δ_2 are 2D Laplace operators, $\rho_{a1}, \rho_{a2}, \rho_{b1}$ and ρ_{b2} are the electron–ion distances and ρ_{12} and R the electron–electron and ion–ion distances, respectively.

A normalized trial function for the ground state of the full Hamiltonian H is:

$$\psi = [a(1)b(2) + b(1)a(2)]/\sqrt{2(1 + S^2)} \qquad (2)$$

where $a(i)$ and $b(i)$ are the normalized wavefunctions of ground states of 2D hydrogen-like atoms (Zaslow and Zandier 1967) located in a and b, respectively:

$$a(i) = \sqrt{(2/\pi)}\alpha\, e^{-\alpha\rho_{ai}} \qquad (3)$$

$$b(i) = \sqrt{(2/\pi)}\alpha\, e^{-\alpha\rho_{bi}} \qquad (4)$$

where α is a variational parameter and S is the overlap integral.

For a given value of the interatomic distance R, the total energy is

$$E(\alpha, R) = \langle\psi|H|\psi\rangle \qquad (5)$$

which can be calculated partly analytically and partly numerically.

$$E(\alpha, R) = \alpha^2 F_1(w) + \alpha F_2(w) + 2/R \qquad (6)$$

where w is equal to αR,

$$F_1(w) = (2 - 2KS - 2S^2)/(1 + S^2) \qquad (7)$$

$$F_2(w) = (-8 + 4J + 2J' + 8KS + 2K')/(1 + S^2). \qquad (8)$$

Using modified Bessel functions of orders zero and one, we can respectively express S, K and J as

$$S = w^2\left[\tfrac{1}{2}K_0(w) + (1/w)K_1(w)\right] \qquad (9)$$

$$K = -2wK_1(w) \qquad (10)$$

$$J = 2w(K_0(w)I_1(w) - K_1(w)I_0(w)). \qquad (11)$$

J', related to the Coulomb interaction between two electrons, can be calculated analytically by using the addition theorem of Bessel functions and the relation

$$1/\rho_{12} = \sum_{m=-\infty}^{\infty} \int_0^{\infty} dk\ e^{im(\varphi_{2a}-\varphi_{1a})} J_m(k\rho_{2a}) J_m(k\rho_{1a}) \qquad (12)$$

and is as follows:

$$J' = (3\pi/8)\,_1F_2\left(\tfrac{1}{2}; -\tfrac{3}{2}, 1; w^2\right) - (64w^5/225)\,_1F_2\left(3; \tfrac{7}{2}, \tfrac{7}{2}; w^2\right) \qquad (13)$$

where $_1F_2(\alpha; \beta, \gamma; z)$ is the generalized hypergeometric function. However, K' related to the exchange interaction between two electrons cannot be calculated analytically and a numerical integral method should be used.

The parameter α is determined by minimizing $E(\alpha, R)$ and is given by

$$\alpha = -[F_2(w) + wF_2'(w)]/[2F_1(w) + wF_1'(w)] \qquad (14)$$

where $F_1'(w)$ and $F_2'(w)$ are the derivatives of $F_1(w)$ and $F_2(w)$, respectively. Once α is known, the ground-state energy of 2DHM can be obtained for R, which equals w divided by α. Then, the binding energy takes the form

$$E_B(R) = -8 - E_g(R) \qquad (15)$$

where $E_g(R)$ is the ground-state energy (including the potential energy between the ions) of 2DHM.

Table 1. Variational parameter α, ground-state energy E (excluding the inter-ion potential) and binding energy E_B of a 2DHM with the corresponding R and w. The equilibrium distance is 0.3682. All values are given in atomic units.

R	α	w	E	E_B
0	3.411	0	−23.269	
0.0943	3.182	0.3	−21.297	−7.912
0.2086	2.876	0.6	−18.664	1.076
0.3481	2.585	0.9	−16.131	2.386
0.3682	2.550	0.939	−15.828	2.396
0.5115	2.346	1.2	−14.026	2.116
0.6876	2.181	1.5	−12.465	1.557
0.9782	2.045	2.0	−10.765	0.808
1.500	2.000	3.0	−9.516	0.183
2.000	2.000	4.0	−9.035	0.0349
2.500	2.000	5.0	−8.805	0.0051
3.000	2.000	6.0	−8.666	0.00031

The functions S, J, K, J' and K' and their derivatives have been calculated for w ranging from one to six. Using (6)–(8), (14) and (15), we can obtain the variational parameter α, the ground-state energy and the binding energy of a 2DHM for the corresponding value of R as shown in table 1. In this table, it is shown that the α decreases monotonically from 3.411 to 2.00 and the ground-state energy (excluding the potential energy between the ions) from −23.269 (2D helium) to −8 Ryd (two

2D hydrogen atoms) as R increases from zero to a large value. The binding energy increases and approaches the maximum 2.396 Ryd as R decreases from a large value to 0.3682 Bohr, and then decreases. It is easier to understand that the binding energy and the equilibrium distance of a 2DHM are, respectively, larger and shorter than those (1.646 Ryd and 0.511 Bohr of a 2D hydrogen molecular ion (HMI) as first obtained by Zhu and Xiong (1990). It is interesting to note that the binding energy of a 2DHM is about eight times as large as that of a three dimensional (3D) HM while the equilibrium distance of a 3DHM is about four times as large as that of a 2DHM. Comparing the differences of the binding energy and equilibrium distance of a HM between 2D and 3D cases with the corresponding ones of an EM between different σ, we can conclude that the dimensionality effect on EMs in semiconductors is as important as that of the electron and hole effective-mass differences. Therefore, we should consider both of the dimensionality and the effective-mass ratio effects for the studies of EMs in QWs. If we assume that there are near similar σ-dependences of the binding energy and the mean inter-hole distance between EMs of different dimensions, we can estimate the binding energy and the EM mean distance in low-dimensional conditions by using the results of the corresponding low-dimensional HMs and 3DEMs. However, it should be interesting to study the 2DEM σ-dependences. This work is in progress.

In conclusion, we have obtained the variational solution of the ground state of a 2DHM and have given the numerical results of the ground-state energy and the binding energy. It is shown that the binding energy and equilibrium distance for 2DHMs are respectively larger and shorter than those for 2DHMIs, and much larger and shorter than those for 3DHMs. According to the properties of 2DHM, we have concluded that the dimensionality effect on EMs in semiconductors is important. Therefore, it is worthwhile to study the behaviour of EMs in QWs considering both the dimensionality and effective-mass ratio effects. It is also worthwhile to point out that better results for a 2DHM can be obtained if the covalent–ionic configuration mixing and the electron correlation in trial functions are considered. Finally, we should point out that the shorter equilibrium distances in low-dimensional HMIs and HMs may be one reason why the probability of finding two deuteriums at zero separation (Jones 1986) can be significantly increased when a large number of deuterium molecules are loaded into a metal or some other form of condensed matter.

References

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