Possibility of Exciton Binding to Ionized Impurities in Semiconductors

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THE possible binding of excitons to ionized impurities in semiconductors has been considered by Sharma and Rodriguez,[1] that is the formation of donor-hole or acceptor-electron complexes. The exciton is simply treated as consisting of a hole and an electron with masses m_h and m_e, respectively. For definiteness, we consider the case of an ionized *donor*, the results being valid for an acceptor, provided the electron and the hole have their roles exchanged. The crucial question is, For what values of the mass ratio $\sigma=m_e/m_h$ does a bound state exist? Sharma and Rodriguez claim that $\sigma\geq 4$. The purpose of this paper is to point out that the second region does not exist and that the first region may be enlarged, using results previously known. Indeed, an analogous three-body Coulomb problem has already been investigated in atomic physics while studying the binding of a positron to an hydrogen atom (system pe^-e^+).

I first show that there cannot be two disjoint regions for σ where bound states exist. In fact, binding results when the ground-state energy $E(\sigma)$ of the Hamiltonian:

$$H=\frac{\mathbf{P}_e^2}{2m_e}+\sigma\frac{\mathbf{P}_h^2}{2m_e}-\frac{e^2}{Kr_e}+\frac{e^2}{Kr_h}-\frac{e^2}{K|\mathbf{r}_h-\mathbf{r}_e|},$$

is lower than the binding energy $E_0=-m_ee^4/2K^2\hbar^2$ of the donor (ion + electron). Now, according to the so-called Feynman-Hellman theorem,[2]

$$\frac{dE}{d\sigma}=\left\langle\frac{\partial H}{\partial\sigma}\right\rangle=\left\langle\frac{\mathbf{P}_h^2}{2m_h}\right\rangle\geq 0,$$

where the average is taken with respect to the true ground-state wave function. $E(\sigma)$, then is a monotonously increasing function.[3] Calling σ_c the critical mass ratio such that $E(\sigma_c)=E_0$, and which will be shown to exist, there is but one binding region, $0\leq\sigma\leq\sigma_c$.

For $\sigma=0(m_h=\infty)$, the system is identical to the bound molecular ion H_2^+ and $E(0)\simeq 1.2E_0$.[4] On the other hand, for $\sigma\gg 1$, the electron is much more massive than the hole and moves quite close to the ionized impurity, so that the hole, too remote, sees but an over-all neutral donor and cannot be bound. This crude argument, suggesting a finite value of order unity for σ_c, is substantiated by the results of Gertler, Snodgrass, and Spruch.[5] Using an adiabatic technique to obtain lower bounds to the ground-state energy, hence necessary conditions for binding, they show that $\sigma_c\leq 1.33$. The binding region $\sigma\geq 4$ of Sharma and Rodriguez thus does not exist.

Furthermore, their result $\sigma_c\geq 0.20$ was already superseded by a result due to Frost, Inokuti, and Lowe.[6] Using the variational principle as do Sharma and Rodriguez, but with a more refined trial function, these authors have shown that $\sigma_c\geq 0.383$. The exact value for σ_c probably lies close to this limit, since the trial wave function seems pretty accurate. It is a difficult problem to obtain improved lower bounds for $E(\sigma)$, so as to be able to bridge the gap between the quoted upper and lower bounds for σ_c. In particular, the challenge remains to prove that $\sigma_c<1$, that is, an hydrogen atom cannot bind a positron.

Of course, because of the crudeness of the model, the exact value of σ_c is not relevant to the real situation in semiconductors. But what matters is that *there does exist a critical mass ratio $\sigma_c\lesssim 1$, such that an ionized donor (acceptor) cannot bind an exciton if the hole (the electron) is much lighter than the electron (the hole).*

In particular, in CdS an exciton can be attached only to an ionized donor, contrary to Sharma and Rodriguez's conclusions, but in agreement with the observations.[7] Similarly, in GaSb ($\sigma=0.23$), we are led to interpret the observations of Johnson and Fan[8] as due to the existence of exciton-donor complexes, and not to exciton-acceptor complexes as proposed by Sharma and Rodriguez.

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[1] R. R. Sharma and S. Rodriguez, Phys. Rev. **153**, 823 (1967).

[2] See, for example, E. Merzbacher, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), Ex. 16.9.

[3] In fact, a similar remark was made by Sharma and Rodriguez themselves, for a related problem: R. R. Sharma and S. Rodriguez, Phys. Rev. **159**, 649 (1968).

[4] The known expression for the ground-state energy of H_2^+ can be scaled so as to give an estimate of $E(\sigma)$ for $\sigma\ll 1$. See J. J. Hopfield, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris 1964* (Dunod, Paris, 1964), p. 725.

[5] F. H. Gertler, H. B. Snodgrass, and L. Spurch, Proceedings of the Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, 1967, p. 104 (unpublished); Phys. Rev. (to be published).

[6] A. A. Frost, M. Inokuti, and J. P. Lowe, J. Chem. Phys. **41**, 1646 (1964).

[7] C. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. **19**, 574 (1951); D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962); D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Status Solidi **12**, 3 (1965).

[8] E. J. Johnson and H. Y. Fan, Phys. Rev. **139**, M1991 (1965).