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Variational calculation of multihole binding energies in hydrogenic impurity centers in semiconductors

Yan Wu and L. M. Falicov

Department of Physics, University of California, Berkeley, California 94720

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Variational calculations for the binding energies of additionally charged, multiple acceptors in semiconductors, with configurations $(1s)^3$ and $(1s)^4$, are presented.

Recent experiments in very pure semiconductors have renewed interest in the existence and properties of overcharged impurity centers, i.e., negatively charged donors¹⁻⁷ and positively charged acceptors.^{2,3} In addition to the doubly occupied, single donors D^- (e.g., Sb^- in Ge) and single acceptors A^+ (e.g., Ga^+ in Ge), new species of triply occupied, double acceptors (e.g., Be^+ in Ge) and quadruply occupied, triple acceptors (e.g., Cu^+ in Ge) have been reported.⁸ It is important to realize that the atomic equivalent of the usual overcharged centers is H^- (nuclear charge $Z=1$), but the newly reported centers are the analogs of either He^- (nuclear charge $Z=2$) or Li^- (nuclear charge $Z=3$) ions.

The simple theory for A , D , A^+ , and D^- is based on atomlike models, essentially identical to the H-atom systems, with an effective mass m^* and a dielectric constant ϵ characteristic of the semiconductor. The He-like and Li-like analogs are, however, very different, since the Pauli exclusion principle forbids the existence of the $(1s)^3$ and $(1s)^4$ configurations. In the case of acceptors in Ge, these configurations are possible because of the fourfold degeneracy of the top of the valence band, which allows up to four holes to occupy a single one-particle orbital. We therefore extend our atomic analogy to this new situation and talk in terms of pseudoatoms.⁹

For an oversimplified picture of noninteracting carriers, each hole would see only the effective nuclear charge, i.e., $-2|e|$ in the case of Be, Mg, and Zn in germanium, and $-3|e|$ in the case of Cu in germanium. This naive picture would give a total binding energy¹⁰ of 6 a.u. for Be^+ and 18 a.u. for Cu^+ . Such large energies are unphysical, since they neglect the strong hole-hole interactions which are very large, of the same order of magnitude as the quoted numbers. Whether and by how much an extra hole binds to a neutral multiple acceptor remains a question to be answered, and the one we address here.

We have attempted several simple variational calculations. In all cases we assumed a ground-state function fully symmetric in real space (antisymmetric in the spin degrees of freedom) and with a small number of variational parameters. All our results are summarized in Table I.

A. Single-exponential form

If we assume the variational function to be

$$\psi_1(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \exp[-\alpha(r_1 + r_2 + \dots + r_n)] \quad (1)$$

where there is a single variational parameter α , the calcula-

TABLE I. Variational binding energies for multielectron pseudoatoms. All energies in a.u.

Z	n	Independent particles	Single exponential	Multiple exponential	Multiple exponential with $\cos\theta_{ij}$ correlations	Double exponential with r_{12} correlations
1	2	-1.000	-0.473	-0.513	-0.517	-0.526
2	2	-4.000	-2.848	-2.876	-2.885	-2.901
2	3	-6.000	-2.836	-2.988	-3.006	
3	2	-9.000	-7.223	-7.249	-7.259	-7.277
3	3	-13.500	-8.461	-8.591	-8.617	
3	4	-18.000	-8.508	-8.925	-8.945	

tion is very simple and described in detail in textbooks.¹¹ It yields unbounded states for both H^- and pseudo He^- , although it gives a small binding energy for pseudo Li^- (0.047 a.u.). For a nuclear charge Z and n electrons (or holes), the variational parameter α takes the values

$$\alpha(Z, n) = Z - \frac{5}{16}(n-1), \quad (2)$$

with

$$E(Z, n) = -n\alpha^2/2. \quad (3)$$

B. Multiple-exponential form

If we increase the number of variational parameters to n , the number of "electrons," we may choose a function of the form¹²

$$\psi_2(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \hat{S} \exp\left[-\sum_i \alpha_i r_i\right], \quad (4)$$

where \hat{S} is the symmetrizing operator. In this case all three additionally charged ions are bound: H^- (0.013 a.u.), pseudo He^- (0.112 a.u.), and pseudo Li^- (0.334 a.u.). We obtain the following variational exponents:¹²

$Z=1, n=2:$	1.039;	0.283.	
$Z=2, n=2:$	2.181;	1.195.	
$Z=3, n=2:$	3.291;	2.081.	
$Z=2, n=3:$	2.276;	1.219;	0.579.
$Z=3, n=3:$	3.540;	2.086;	1.486.
$Z=3, n=4:$	3.600;	2.290;	1.447; 0.818.

C. Angular-correlation form

It is possible to include electron-electron angular correlations by adding one additional parameter C to the multiple-exponential form

$$\Psi_3(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) = \psi_2(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \left[1 + C \sum_{i < j} \cos\theta_{ij}\right] \quad (5)$$

All necessary integrals can be performed analytically and only the parameter minimization requires numerical calculation. The results, as shown in Table I, show binding energies of 0.017 a.u. for H^- , 0.121 a.u. for pseudo He^- , and 0.328 a.u. for pseudo Li^- .

It is interesting to see that even though the binding of the

additional electron increases with nuclear charge in all approximations, the addition of angular correlations yields very small corrections and, surprisingly, decreases¹³ the binding energy of Li^- .

It is also worth noticing that the best value obtained for the total energy of H^- (-0.5276 a.u.) gives an error of 38% in our estimate of the binding energy. The ionization energy of He is obtained, however, with an accuracy of 2%.

The variational parameter C is, in general, very small, but its nonzero value also changes slightly the values of α_i . For example,

$$Z=2, n=2: \alpha_1=2.171; \alpha_2=1.198; C=0.048.$$

These values should be compared with those for α_i quoted above.

D. Particle-separation correlation form

Although it is of no use for pseudo He^- and pseudo Li^- , we have, for two electrons, tried a better approximation:¹²

$$\Psi_4(\vec{r}_1, \vec{r}_2) = \Psi_2(\vec{r}_1, \vec{r}_2)(1 + D r_{12}), \quad (6)$$

which yields for H^- , He^0 , and Li^+ excellent results (see table). In particular, the ionization energy of He is accurate to 3 parts in 1000, and the binding energy of H^- to 5%. The changes in the α_i parameters, however, are still small.

$$Z=2, n=2: \alpha_1=2.205; \alpha_2=1.445; D=0.300.$$

In conclusion, we would like to remark that (a) multiple acceptors in semiconductors should bind an extra hole in all cases ($Z=2$ and $Z=3$), (b) the binding energies should be of the order of a few tens of the relevant atomic energy unit, i.e., a few meV, and (c) variational calculations, which are extremely simple, yield very acceptable results.

Improvements to our theory can be easily achieved on many fronts: (i) by taking into account more accurately the details of the semiconductor valence-band structure, e.g., the presence of two masses; (ii) by including central-cell corrections; and (iii) by going into more sophisticated Green's-function methods.^{14,15}

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⁹For acceptors, the fourfold degeneracy of the top of the valence band can be cast, for impurity centers, into a picture of atoms with spin- $\frac{3}{2}$ electrons.

¹⁰Throughout this paper our energy units are effective Hartree atomic units, 1 a.u. = $m^*e^4/\epsilon^2\hbar^2$, where m^* is the hole effective mass and ϵ is the semiconductor dielectric constant.

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¹³There is, of course, no violation of the variational principle: The addition of the extra parameter C decreases the total energies of both Li^0 and Li^- , but more of the former than of the latter and thus reduces the binding energy of Li^- .

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