Classification

Physics Abstracts

71.55F — 78.55D

Binding to a pair of marginal potentials : a test for the stability of N^- in GaP

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(Reçu le 17 septembre 1982, révisé le 12 novembre, accepté le 16 novembre 1982)

Résumé. — On montre que le comportement des paires distantes NN^- fournit un test de stabilité de N^- . On propose une méthode améliorée de calcul de l'énergie de NN^- , ainsi que du comportement asymptotique à grande distance R pour un potentiel près de la limite de liaison. On démontre que l'énergie de liaison à une paire de potentiels « marginaux » est une fonction universelle de R , et indépendante de la nature du potentiel. On conclut que N^- n'est pas stable dans GaP.

Abstract. — It is shown that a test for the stability of N^- can be found from the behaviour of pairs NN_i^- at large separation. An improved method of calculation of the energy of NN_i^- is presented and its asymptotic behaviour at large pair separation R is obtained for potential near the limit of vanishing binding. It is shown that the binding energy to a pair of « marginal » potentials is a universal function of R , independent of the nature of the potential. It is concluded that N^- is unstable in GaP.

1. **Introduction.** — N substituted to P in GaP is the most thoroughly studied shallow isoelectronic centre [1]. N being more electronegative than P causes an attractive short-range potential for the electron [2] but one does not know if N^- is stable or not in GaP. In this paper, we propose to find a test of stability of N^- from the study of NN_i^- , an electron bound to a pair of nitrogen ; good experimental data about NN_i^- have been obtained by Cohen and Sturge [3] from excitation spectroscopy of the luminescence of excitons bound to pairs. Here, we propose an improved method, yet very simple, to compute the ground state of NN_i^- as a function of the pair separation and the depth of the localized isoelectronic potential. In addition, we found an asymptotic law for the binding energy E to a pair of « marginal » potentials at large pair separation R : $ER^2 = \text{const.}$, independent of the nature of the potential. A simple test for N^- stability is derived.

2. **Theoretical calculation of NN_i^- ground state.** — Let $V(r)$ the isoelectronic potential spherically symmetric. It is assumed of constant shape but with a prefactor $(1 + \varepsilon)$. $V(r)$ is chosen such that being short-range, the binding energy of the electron is just vanishing : this is our definition of a « marginal » potential. Actual potential $(1 + \varepsilon)V(r)$ has a ground state of energy $E(\varepsilon)$ for $\varepsilon > 0$.

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For a pair at separation R , we use a variational method, with a trial wave function of the bonding type :

$$\Psi = (\phi_{1\eta} + \phi_{2\eta})/\sqrt{2}, \quad (1)$$

$\phi_{i\eta}$, centred on impurity i ($i = 1, 2$) is the solution for a potential $(1 + \eta) V(r)$:

$$[K + (1 + \eta) V(r) - E(\eta)] \phi_{\eta} = 0, \quad (2)$$

where η is the variational parameter.

This trial wave function is exact in the two limiting cases $R = 0$ where $1 + \eta = 2(1 + \varepsilon)$ give the solution, and $R \rightarrow \infty$ where $\eta = \varepsilon$. Thus it is expected to be quite good at any value of R ; it gives much better results than the choice $\phi \sim \exp(-r/a)$ as used in [4]. The variational energy E_1 is :

$$E_1 = E(\eta) + [(1 + \varepsilon)(B + C) + (\varepsilon - \eta)(A + B)]/(1 + D) \quad (3)$$

where

$$\begin{aligned} A &= \int \phi_{1\eta} V_1 \phi_{1\eta} d^3r & B &= \int \phi_{1\eta} V_1 \phi_{2\eta} d^3r \\ C &= \int \phi_{1\eta} V_2 \phi_{1\eta} d^3r & D &= \int \phi_{1\eta} \phi_{2\eta} d^3r. \end{aligned}$$

Numerical calculations as a function of ε and R have been performed in the case of a square well potential : $V(r) = \frac{-\pi^2}{4b^2}$ for $r < b$, $V(r) = 0$ for $r > b$ (b is the radius of the localized potential).

The results are shown in Section 4.

We find that the minimum E_{1m} of E_1 is obtained for a value $\eta = \eta_m$ such that $E_{1m} \sim E(\eta_m)$. This is not surprising for the following reason : outside the two localized potentials, the ground state wave function of NN^- is a linear combination of plane waves of energy E_0 , where E_0 is the ground state energy. The ansatz (1) outside the two localized potentials is also a linear combination of plane waves of energy $E(\eta)$. If (1) is a good ansatz, then clearly one should have $E_0 = E(\eta_m)$.

3. Asymptotic behaviour. — We consider the case $\varepsilon = 0$, $R \rightarrow \infty$. Since the ansatz (1) is exact at $R \rightarrow \infty$, we can use the « physical » argument of the end of Section 2 and replace the minimization of E_1 , by $E_1 = E(\eta)$ in equation (3), hence

$$(1 + \varepsilon)(B + C) + (\varepsilon - \eta)(A + B) = 0. \quad (4)$$

Indeed, we show in the appendix that we can arrive at the same result by a direct (but more tedious) derivation from equation (3). We take $\hbar = m = 1$.

To evaluate A , B and C , we consider $f_0 = r\phi_0$; f_0 is solution of

$$\frac{d^2 f_0}{dr^2} = V f_0. \quad (5)$$

The normalization is chosen such that $f_0 = 1$ at $r \rightarrow \infty$. For a small η , f_{η} is essentially equal to f_0 inside the potential, and like $\exp(-kr)$ outside the potential, where $k = \sqrt{-E(\eta)}$. To normalize

ϕ_η as usually, the main contribution comes from the region outside the potential, introducing a factor $N^2 = \frac{k}{2\Pi}$. So we have

$$\begin{aligned}\phi_\eta &= N f_0 / r && \text{inside the potential,} \\ \phi_\eta &= N \exp(-kr) / r && \text{outside the potential.}\end{aligned}\quad (6)$$

Then one obtains

$$\begin{aligned}A &= 2kI_A \\ B &= 2kI_B \exp(-kR)/R \\ C &= 2kI_C \exp(-2kR)/R^2,\end{aligned}\quad (7)$$

where

$$I_A = \int f_0^2 V \, dr \quad I_B = \int r f_0 V \, dr$$

and

$$I_C = \int r^2 V \, dr.$$

I_A^{-1} has the dimension of a length. It can be considered as the « effective » radius of the marginal potential (for a square well : $I_A^{-1} = -8b/\Pi^2$).

I_B can be computed using (5)

$$\begin{aligned}I_B &= \int r \frac{d^2 f_0}{dr^2} \, dr = \int \frac{d}{dr} \left(r \frac{df_0}{dr} - f_0 \right) \, dr = \left| r \frac{df_0}{dr} - f_0 \right|_0^\infty, \\ I_B &= -1 \text{ provided } r \frac{df_0}{dr} = 0 \text{ when } r \rightarrow \infty.\end{aligned}$$

This condition does not introduce any limitation on V for the following reason : if when $r \rightarrow \infty$, $f_0 = 1 - ur^{-s}$ then $r \frac{df_0}{dr} \sim r^{-s}$ and $V \sim r^{-(s+2)}$, $r \frac{df_0}{dr} \rightarrow 0$ if $s > 0$, and so V should decay faster than r^{-2} . This is a necessary condition for a marginal potential [5].

I_C has the dimension of a length ($I_C = -\Pi^2 b/12$ for a square well). The approximate way we have computed C implies that V should decay faster than r^{-3} .

For large R , (6) show that $A \gg B \gg C$. This comes from the power dependence in R , and not from the exponential term, because at the end it happens that kR remains finite.

For $\varepsilon = 0$, equation (4) reduces to

$$B - \eta A = 0. \quad (8)$$

Now, from the differentiation of equation (2) we get $A = \frac{dE(\eta)}{d\eta}$ hence, using (7) and $E(\eta) = -k^2$,

$$I_A = -\frac{dk}{d\eta}, \quad \text{then } k = -I_A \eta,$$

since $k = 0$ at $\eta = 0$.

Then (8) becomes

$$\exp(-kR) = kR. \quad (9)$$

The numerical result is $kR = 0.567$ or

$$E = -0.322/R^2. \quad (10)$$

Thus, the binding of a particle to a pair of « marginal » potentials is, at large pair separation, a universal function of R , independent of the nature of the potential.

For ε small, (4) can be approximated as

$$kR + \varepsilon I_A R = \exp(-kR). \quad (11)$$

This shows that the relevant parameter to measure a distance to the « marginal » case is εI_A (rather than ε). In particular, if $\varepsilon < 0$ the distance R_0 at which the binding to a pair vanishes is

$$R_0 = 1/(\varepsilon I_A). \quad (12)$$

4. Comparison with N in GaP. — Figure 1 gives the results of NN^- ground state energy calculation for a square well potential, as a function of R and for five values of ε (from -10% to 10%). The asymptotic law (10) has also been drawn. On the same graph, we have plotted the experimental points coming from reference [3]. The only parameter of interest is the electron effective mass in GaP. Since we are interested in very shallow states, there is no ambiguity. We have taken $m^* = 0.5$, which gives associated with $K = 11$ an electron Rydberg of 55 meV (the energy of the valley orbit splitted states of the donor). In reference [3], Cohen and Sturge measure the excitation spectrum of the luminescence of an exciton bound to a pair NN_i . The pair separation is $R_i = d\sqrt{i/2}$, where d is the lattice constant ($\sim 5.4 \text{ \AA}$ in GaP). The excited states correspond to nS orbitals of the hole wave function. The ionization limit, corresponding to NN_i^- , is obtained by an extrapolation procedure, the binding energy of NN_i^- is $E_{\text{Gap}} - E_{\text{NN}_i^-}$.

Fig. 1. — Log-Log plot of the pair separation R versus the binding energy of NN^- for different values of ε (-10% , -5% , 0 , 5% , 10%). The experimental points correspond to NN_i^- in GaP ($i = 1$ to 7).

In indirect gap semiconductors an accurate value of E_{Gap} is difficult to obtain. The data known accurately is the energy of the bottom of the free exciton band. Here, we have taken a value of the exciton Rydberg of 20 meV, the error being estimated to ± 2 meV. This error would affect to some extent the position of the points $i = 5$ to 7 and the log-log plot of figure 1, but it would not affect the main conclusion : the experimental points at large R ($i = 4$ to 7) are clearly on the left of the asymptote. This shows unambiguously that $\varepsilon < 0$ for N in GaP. Also the slope at large R is fairly well accounted for by our theory. The experimental slope approaching a R^{-3} law [6] is

also typical of a region $\varepsilon \sim -0.08$, and has nothing to do with a particular shape of the isoelectronic potential. From (12) one can evaluate the separation R at which the binding of NN^- vanishes. One finds $R \sim 24 \text{ \AA}$ ($i \sim 40$). Let us recall why the experimental data stop at $i = 7$. This is because the nS excited states are broadened when they are in resonance with the free exciton continuum.

In figure 1, the theoretical curves were computed with a radius $b = 2.4 \text{ \AA}$. Changing b would just move the theoretical curves parallel to the R^{-2} asymptote. This corresponds to the fact that the relevant parameter of the N isoelectronic potential we can extract is εI_A , which is about $0.04 \text{ \AA}^{-1}$. For E_{NN^-} larger than 40 meV, the model based on a simple parabolic band structure is no longer accurate. The deviation for $i = 3, 2$ is equivalent to an increase of m^* for deeper levels. The very peculiar situation of NN_1 could be related, we believe, to an overlap of the potentials of the two impurities, producing some non-linear effect. This is the only reason why we choose a value of b such that $2b$ is between the pair separation in NN_1 and NN_2 . However, a smaller value of b ($\sim 1.5 \text{ \AA}$) is predicted in first principle theoretical calculation of isoelectronic potentials (2).

5. Conclusion. — We have shown that for an isoelectronic potential near the limit of vanishing binding, the study of pairs (NN_i) provides an unambiguous test for the stability of N^- . This procedure is not sensitive to the exact shape of the electronic potential. On the other hand, one can try to deduce the stability of N^- from the known binding energy of the exciton bound to N. An attempt to do it through a simple Hartree self-consistent method has predicted a positive value of ε [7]. This simply points out the necessity to include electron-hole correlation in such calculations.

Acknowledgments. — I thank P. Nozières for his encouragement and critics.

Appendix. — To deduce formally (4) from (3), we have to compute the overlap integral D . We assume that, at large R and small η , the main part comes from the region outside the potentials. Then from (6)

$$D = \frac{k}{2\pi} \int d\tau \frac{e^{-k(r_1+r_2)}}{r_1 r_2}.$$

The volume element is $d\tau = \frac{r_1 r_2}{R} dr_1 dr_2 d\varphi$ and in the quadrant $r_1 r_2$ the domain of integration is limited by $r_1 + r_2 > R$ and $|r_1 - r_2| < R$

$$D = \frac{k}{R} \int dr_1 dr_2 e^{-k(r_1+r_2)}.$$

Using $r_1 + r_2 = x$ and $r_1 - r_2 = y$

$$D = \frac{k}{2R} \int_{-R}^R dy \int_R^\infty dx e^{-kx} = e^{-kR}. \quad (13)$$

Retaining the main significant terms in (3) we obtain :

$$E_1 = E(\eta) + \frac{B - \eta A}{1 + D}.$$

Using (7), (13) and the definition of k

$$E_1 = -k^2 + \frac{2k}{R} \frac{kR - \exp(-kR)}{1 + \exp(-kR)}.$$

Differentiation with respect to k gives

$$[kR - \exp(-kR)] \frac{1 + \exp(-kR) + kR \exp(-kR)}{[1 + \exp(-kR)]^2} = 0,$$

which is equivalent to (9).

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