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**LETTER TO THE EDITOR**

# $D^-$ centres in low dimensions: the strong-confinement approach

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**Abstract.** Negatively charged centres ($D^-$) formed in semiconductors by attaching a second electron to a shallow neutral hydrogenic donor ($D^0$) have been analysed in the quasi-zero- and quasi-one-dimensional limits. On the basis of the present and already known results for higher dimensions, it is proposed that $D^-$ ions support one and only one stable configuration which evolves continuously from the three-dimensional to the zero-dimensional limit.

The interplay between the lowering of one of the physical dimensions in semiconductor heterostructures and the behaviour of shallow impurities immersed in these quasi-two-dimensional artificial solids proved to be quite fruitful in the last decade, a prime example being their binding energy dependence on quantum well size and impurity position [1]. While most of this work concentrates on neutral donor and acceptor configurations, negatively charged donor centres (the solid-state analogue of the $H^-$ ion of atomic physics) have recently received increasing attention. Huant *et al* [2] have identified $D^-$ states in a quasi-two-dimensional environment of a GaAs quantum well surrounded by $Al_xGa_{1-x}As$ barriers. This report was followed by other experimental [3] and theoretical [4, 5] works.

Motivated by these results and the advance in confinement techniques, which opens the way to the fabrication of quasi-one-dimensional (quantum wires (QW)) and quasi-zero-dimensional (quantum dots (QD)) dynamically confined systems, the question of the number of stable configurations (bound states) of $D^-$ centres in low dimensions arises. This question has a rigorous answer in 3D, where according to the Hill theorem [6], the $D^-$ ion supports one and only one bound singlet state. In 2D, while to the best of our knowledge no equivalent rigorous proof exists, from all the above-quoted experiments and calculations growing evidence builds of the existence of only one bound state.

We provide in this letter strong evidence that a negatively charged hydrogenic donor impurity supports one and only one stable configuration in any of the physically accessible dimensions. The theoretical models that we use are idealized, as we are interested more in conceptual than in quantitative results; we begin with the QD case.

(a) *Quantum dot.* The Hamiltonian for a $D^-$ centre within a spherical quantum well with infinite barriers can be written as the sum of the kinetic energy

$$-\frac{1}{\lambda^2}(\nabla_1^2 + \nabla_2^2) \equiv \frac{1}{\lambda^2} H_0 \tag{1}$$

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and the Coulomb interactions among both electrons and the impurity

$$-\frac{1}{\lambda}[U(\boldsymbol{r}_1, \boldsymbol{r}_i) + U(\boldsymbol{r}_2, \boldsymbol{r}_i) - U(\boldsymbol{r}_1, \boldsymbol{r}_2)] \equiv -\frac{1}{\lambda} V \tag{2}$$

where $\lambda = R/a_0^*$ ($R$ and $a_0^*$ being the dot and effective Bohr radius, respectively), $\boldsymbol{r}_1, \boldsymbol{r}_2$ ($\boldsymbol{r}_i$) are the electron (impurity) coordinates, $\nabla_1^2$ and $\nabla_2^2$ are 3D Laplacians, and $U(\boldsymbol{r}, \boldsymbol{r}') = 2/|\boldsymbol{r} - \boldsymbol{r}'|$. In writing equations (1) and (2), we use the effective Rydberg $R^* = m^* e^4 / 2\hbar^2 \epsilon^2$ as the energy unit (with $m^*$ and $\epsilon$ the effective mass and dielectric constant of the semiconductor well acting material) and $R$ as the length unit.

The kinetic energy and Coulomb interactions scale like $\lambda^{-2}$ and $\lambda^{-1}$, respectively. Thus the former dominates at small $\lambda$. In this strong-confinement limit, the Coulomb interactions of equation (2) can be treated by standard perturbation theory, using the eigenfunctions of $H_0$ as zero-order solutions. This technique was applied in [7, 8, 9] to study the stability of biexcitons in semiconductor quantum dots.

The zero-order wave functions are the products of the one-particle kinetic energy eigenfunctions in the sphere $\psi(\boldsymbol{r})$ with the boundary condition $\psi(\boldsymbol{r})_{r=1} = 0$. The solutions finite at the origin are $\psi_{n\ell m}(\boldsymbol{r}) = N_{n\ell} j_\ell(kr) Y_{\ell m}(\theta, \phi)$ with energy $E = k^2$; $N_{n\ell}$ is a normalization constant, $j_\ell(kr)$ are the spherical Bessel functions, and $Y_{\ell m}$ are the spherical harmonics. The wave function must vanish at the boundary $j_\ell(k) = 0$ giving the eigenvalue spectrum $k_{n\ell} = x_{n\ell}$ where $x_{n\ell}$ is the $n$th zero of the $\ell$th spherical Bessel function [10]. The normalization integral can be evaluated to give $N_{n\ell}^2 = 2/j_{\ell+1}^2(x_{n\ell})$.

We define the binding energy of the $\mathrm{D}^-$ centres as

$$E_B = (E_{\mathrm{D}^0} + E_0) - E_{\mathrm{D}^-} \tag{3}$$

where the first two terms represent the energy of the ‘unbound’ configuration, with an electron attached to the impurity in the neutral configuration ($E_{\mathrm{D}^0}$), and the second electron in the lowest available energy state for a free electron in the quantum dot ($E_0$). The last term corresponds to the ‘bound’ configuration, with both electrons attached to the impurity. The use of quotes reflects the fact that in a 0D situation there is no continuum (unlike for higher-dimensionality cases) and all states are spatially localized, making the physical meaning of the ‘unbound’ configuration unclear; accordingly, let us try to explain this point in more detail. Assuming that we have a more or less homogeneous distribution (same size) of quantum dots, with some of them, as a result of doping, containing a donor impurity with its corresponding electron (the $\mathrm{D}^0$ configuration), we ask the following question: if an electron surplus is available to the system [2, 11], will the electrons go to the impurity-occupied dots (forming $\mathrm{D}^-$ centres) or to the empty dots? The response to this fundamental question which pertains to the very existence of 0D $\mathrm{D}^-$ centres is given by equation (3): a positive (negative) sign of $E_B$ implies the stability (instability) of the negatively charged centre against the neutral configuration.

Application of standard perturbation theory for $E_{\mathrm{D}^0}$ and $E_{\mathrm{D}^-}$ up to second order in $\lambda$ yields the following expansion for the binding energy:

$$E_B = \frac{1}{\lambda} E_B^{(1)} + E_B^{(2)} + \mathrm{O}(\lambda). \tag{4}$$

In deriving equation (4) it has been assumed that the zero-order wave function of the neutral configuration corresponds to the single electron in the ground one-particle state $|0\rangle$ (0 stands for the set of quantum numbers ($n = 1, l = 0, m = 0$) describing the one-particle ground state); accordingly, the zero-order wave function of the $\mathrm{D}^-$ configuration has been taken as the two-particle ground state $|0, 0\rangle$. In calculating the binding energy given by equation (3) these zero-order contributions (of order $1/\lambda^2$) cancel, and consequently

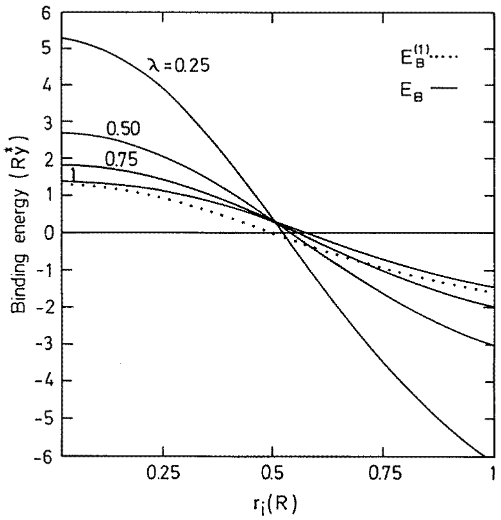

**Figure 1.** The binding energy of D$^-$ centres in quantum dots as a function of impurity position, for several sizes of the quantum dot. The dotted line corresponds to the first-order contribution, while the full lines include the second-order contribution.

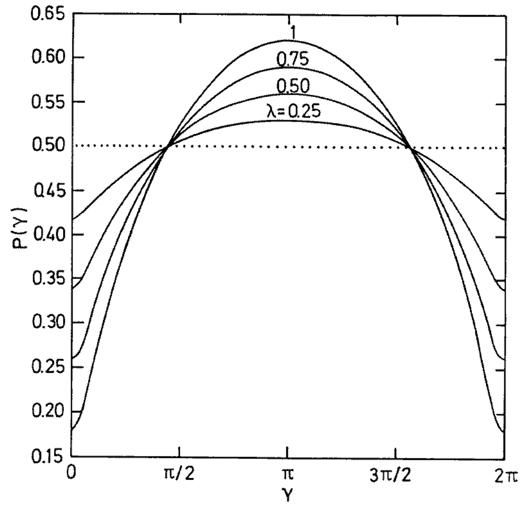

**Figure 2.** The strong angular correlation between the two electrons as revealed by the on-centre impurity radial-integrated probability density $P(\gamma)$ versus the relative angle of the two electrons $\gamma$.

the stability of the D$^-$ centre is determined by potential energy differences, as given by equation (4). Explicit calculations of the one- and two-particle (singlet) ground-state matrix elements of equation (4) yield the following analytic expression:

$$E_B^{(1)}(r_i) = 2\left[\alpha - \frac{\sin(2\pi r_i)}{2\pi r_i} - \mathrm{Cin}(2\pi r_i)\right] \tag{5}$$

with $\alpha \simeq 1.65$ and Cin the cosine integral function [10]. Figure 1 displays the behaviour of $E_B^{(1)}(r_i)$ as a function of the impurity coordinate (dotted line); there exists a critical coordinate $r_i^c$, such that if $r_i < r_i^c$ ($r_i > r_i^c$) the D$^-$ configuration is stable (unstable). From $E_B^{(1)}(r_i) = 0$ we obtain $r_i^c \simeq 0.5$; up to this order, this critical position is independent of $\lambda$. The unbinding reflects the fact that $U(\boldsymbol{r}_1, \boldsymbol{r}_i)$ and $U(\boldsymbol{r}_2, \boldsymbol{r}_i)$ in equation (2) decrease as $\boldsymbol{r}_i$ approaches the boundary (due to the vanishing of the wave function), while the repulsion $U(\boldsymbol{r}_1, \boldsymbol{r}_2)$ remains about the same. In figure 1 we give also the behaviour of the binding energy (equation (4)) for several values of $\lambda$; since the second-order correction is independent of $\lambda$, its importance decreases with $\lambda$, as the first-order correction scales like $1/\lambda$. For the particular case where $r_i = 0$, we obtain $E_B(r_i = 0) \simeq 1.30/\lambda + 0.08$, implying that for the worst case, $\lambda = 1$, the second-order contribution to the binding energy represents a 6% correction to the first-order contribution. From $E_B(r_i) = 0$ we obtain a $\lambda$-dependent $r_i^c$.

From the perturbed wave functions, it is possible to gain some insight into the spatial electronic distribution. As an example, figure 2 shows the $\boldsymbol{r}_i = 0$ probability density integrated over the two radial coordinates, as a function of the relative angle. The dotted line corresponds to the zero-order solution, and obviously no angular correlation exists at this level of approximation. The first-order corrections for several values of $\lambda$ are given by the full lines: an angular correlation exists between the two electrons, as the integrated probability density has a minimum when $\gamma = 0 = 2\pi$ and a maximum when $\gamma = \pi$. This spatial configuration minimizes the Coulomb repulsion between the two electrons and explains the improvement of the binding energy with respect to the zero-order result, for which the binding energy is zero. Similar considerations hold in the 3D, 2D, and 1D (see below) cases, but while in these three cases the binding is the result of angular and radial (with ‘inner’ and ‘outer’ electrons) correlations in the 0D case the binding is essentially given by angular correlations, the radial degrees of freedom being ‘frozen’ in the strong-confinement limit.

The absence of additional stable states arises from equation (4), by assuming for the D$^-$ centre a configuration where one electron is in the ground single-particle state, and the second is in the first excited state (singlet and triplet spin states are allowed in this case). While in the ground-state configuration, a cancellation occurs among the zero-order contributions, no such cancellation occurs in the excited configuration. We obtain a negative zero-order contribution that goes like $1/\lambda^2$ and consequently is the leading contribution to the binding energy in the $\lambda \ll 1$ limit. This result is independent of the spin configuration; differences between singlet and triplet spin states arise in the next order of perturbation. We are led to the rigorous and important conclusion that the D$^-$ ion supports one and only one stable state in the 0D or strong-confinement limit.

(b) *Quantum wire.* In a quasi-one-dimensional situation the simplified model that we use consists of a cylindrical QW with infinite barriers at $\rho = R$, where $R$ is the cylinder radius. Using $a_0^*$ as the unit of length, the Hamiltonian $H = H_0 + V$ can be written as

$$H_0 = -(\nabla_1^2 + \nabla_2^2) \tag{6}$$

$$V = -\left(\frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2}\right) - [U(\boldsymbol{r}_1, \boldsymbol{r}_i) + U(\boldsymbol{r}_2, \boldsymbol{r}_i) - U(\boldsymbol{r}_1, \boldsymbol{r}_2)] \tag{7}$$

where $\nabla^2$ represents now a 3D Laplacian in cylindrical coordinates, but without the $\partial^2/\partial z^2$ term that is included in $V$. This particular distribution of kinetic and interaction terms allows for an approximate separability of the interacting two-electron wave function in the quasi-one-dimensional limit $R/a_0^* \ll 1$ . Thus we can approximate the interacting two-electron wave function by $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \simeq f(\rho_1)f(\rho_2)\phi(z_1, z_2)$, where $f(\rho) = J_0(\alpha_0\rho/R)$ is

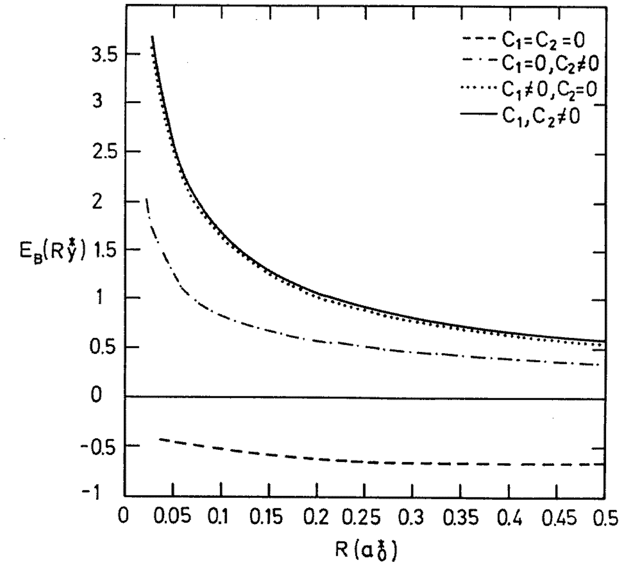

**Figure 3.** The variational binding energy for a $D^-$ centre in a quasi-one-dimensional environment. In the absence of electron–electron correlations in the Chandrasekhar-type trial wave function ($c_1 = c_2 = 0$) the negatively charged configuration is unstable, but when they are incorporated, large binding energies are obtained.

the ground-state solution for $H_0$ which is finite at the origin and satisfies the boundary condition $f(R, \theta) = 0$; $J_0$ is the normalized Bessel function and $\alpha_0$ the first zero of $J_0$.

Elimination of the radial degrees of freedom proceeds now via the calculation of

$$V_{eff}(z_1, z_2) = \int\int \mathrm{d}\rho_1\ \mathrm{d}\rho_2\ \rho_1\rho_2 f(\rho_1) f(\rho_2) V \psi(\boldsymbol{r}_1, \boldsymbol{r}_2) \qquad (8)$$

which produces an effective one-dimensional Schrödinger equation for $\phi(z_1, z_2)$, with effective electron–impurity and electron–electron Coulomb potentials. These are given by integrals over the radial coordinates that should be calculated numerically, resulting in one-dimensional potentials that are finite at the origin.

We have performed a variational solution of (8), using for $\phi(z_1, z_2)$ a generalized singlet Chandrasekhar-type trial wave function [12]

$$\phi(z_1, z_2) = W_\beta(z_1) W_\beta(z_2)[1 + c_1|z_1 - z_2| + c_2|z_1 - z_2|^2] \qquad (9)$$

where $W_\beta(z)$ is the Whittaker function, and $c_1, c_2$ are variational parameters. The Whittaker wave functions are solutions for the one-dimensional hydrogen atom studied by Loudon [13], and depend on the energy-related parameter $\beta$, which in turn depends on the wire radius $R$, through the effective one-dimensional potentials. Equation (9), with $c_1 = c_2 = 0$ is the exact solution of (8) in the absence of effective electron–electron interactions. The rationale behind this variational wave function is that when $c_1$ and $c_2$ are different from zero and positive, the electrons are encouraged to stay apart, decreasing their repulsive interaction energy.

We fitted the numerical electron–impurity and electron–electron potentials of (8) with analytical regularized Coulomb potentials $1/(|z|+a)$ of the type used by Loudon in his study of the 1D hydrogen atom [14]. With these potentials to hand, the calculation of $\beta$ amounts to finding the ground-state solution of the eigenvalue equation of the 1D hydrogen atom.

The energy of the $\mathrm{D}^-$ configuration is given by $E_{\mathrm{D}^-} = \min\langle\phi|V_{eff}|\phi\rangle/\langle\phi|\phi\rangle$, where min represents minimization with respect to $c_1$ and $c_2$. Since according to [13] $E_{\mathrm{D}^0} = -1/\beta^2$, the binding energy is given by $-1/\beta^2 - E_{\mathrm{D}^-}$. While the calculation scheme allows for arbitrary impurity positions, for the sake of simplicity we have restricted ourselves to the on-axis case ($\boldsymbol{r}_i = 0$).

The results for the QW binding energy versus wire radius are given in figure 3: as in the quantum dot case, we found that the binding energy increases monotonically when the wire size decreases. However, and unlike in the previous case, correlations are crucial for the QW. As is seen from figure 3, when $c_1 = c_2 = 0$ and correlation effects are not included in the trial wave function (9) the system is unbounded. Binding occurs as soon as $c_1$ or $c_2$ is variationally optimized, the optimum choice corresponding to the case where both are variationally determined, as expected. The result for $c_1 \neq 0, c_2 = 0$ is quite close to the binding energy for $c_1, c_2 \neq 0$, which makes one confident about the soundness of the series expansion in powers of $|z_1 - z_2|$ implied in equation (9). Furthermore, $c_1$ and $c_2$ increase monotonically when the wire radius decreases (not shown), revealing the increasing importance of electron–electron correlations as the truly one-dimensional limit is reached.

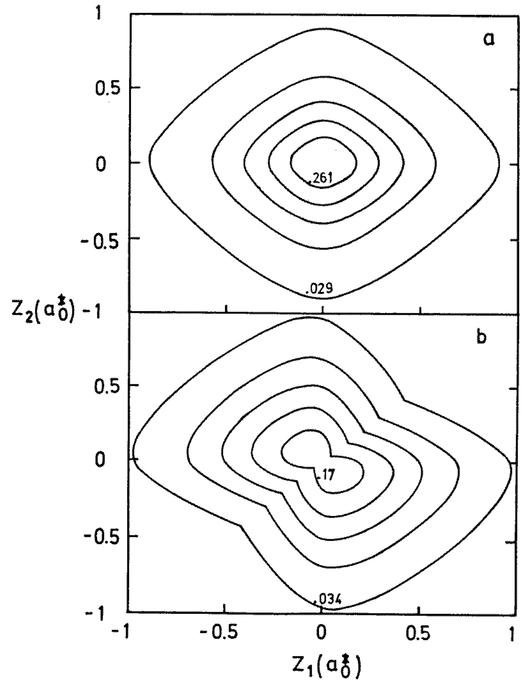

**Figure 4.** Contour plots of the probability density $P(z_1, z_2)$ when $R = a_0^*/2$. Case (a) is for $c_1 = c_2 = 0$, and case (b) for $c_1 \neq c_2 \neq 0$. The inner and outer probability densities are also indicated, the remaining densities being equally spaced between these two values.

The consequences of electron correlations are even more transparent from the contour plots of the probability density $P(z_1, z_2) = |\phi(z_1, z_2)|^2/\langle\phi|\phi\rangle$ shown in figure 4. In the absence of correlations (figure 4(a)), two points should be noticed: first, the probability density along the line $z_1 = z_2$ is exactly the same as that along $z_1 = -z_2$, and second, at lower densities the configuration with $|z_1| \gg |z_2|$ (or vice versa) has a higher probability than that with $|z_1| \simeq |z_2|$. For the highest densities, in contrast, the probability density has an almost perfect rotational symmetry. Dramatic changes are found when correlations are included in the calculation (figure 4(b)): in particular the ‘dip’ at $z_1 = z_2$ reflects the fact that due to Coulomb repulsion the electrons try to avoid each other. The spreading of the probability density is larger than in the previous case, reflecting the fact that the electronic structure of the $D^-$ ion is rather open. Finally, the configuration inner–outer electron is observed even at the highest densities, which is reminiscent of the situation for higher dimensionalities.

Let us compare our results with previous work. Zhu *et al* [15] have studied the problem of $D^-$ centres in spherical quantum dots; using a Chandrasekhar-type trial function they found a singlet stable state. The use of a variational technique made it impossible for them to reach a definite conclusion on the number of stable states; besides, they restrict the calculation to the on-centre impurity case, missing the unbinding found in the present work when $r_i \simeq 0.5$. We are not aware of any calculation on the properties of $D^-$ centres in semiconductor QW. As a final remark, let us emphasize that the results that we found in the present work are qualitatively quite different from those of previous studies of 2D and 3D $D^-$ centres under strong magnetic fields (which can naively be identified with our QD and QW configurations, respectively): *several* bounded states were predicted for 2D $D^-$ centres in the high-magnetic-field limit [5], and it is well known that any finite magnetic field gives rise to an *infinite* number of bound states in the case of 3D $D^-$ centres [16].

In summary, by application of standard perturbation in 0D and variational calculations in 1D we found that the $D^-$ supports a stable state. While the strong-confinement approach to the 0D case allows us to exclude rigorously the possibility of additional stable states, on the basis of our results we cannot eliminate this possibility for the QW. However, on the basis of the well-known results for 3D, and the growing understanding for 2D, we advance the hypothesis that the $D^-$ centre supports only one stable state over the whole range of physical dimensions from 3D to 0D. Quantum-confined semiconductor heterostructures seem to be ideal candidates for the role of testing this prediction.

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## References

[1] Bastard G 1988 *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Ulis: Les Editions de Physique)
[2] Huant S, Najda S P and Etienne B 1990 *Phys. Rev. Lett.* **65** 1486
[3] Mueller E R *et al* 1992 *Phys. Rev. Lett.* **68** 2204
Holmes S *et al* 1992 *Phys. Rev. Lett.* **69** 2571
Cheng J P *et al* 1993 *Phys. Rev. Lett.* **70** 489
[4] Pang T and Louie S 1990 *Phys. Rev. Lett.* **65** 1635
[5] Larsen D M and McCann S Y 1992 *Phys. Rev.* B **45** 3485
Dzyubenko A B 1992 *Phys. Lett.* **165A** 357
Sandler N P and Proetto C R 1992 *Phys. Rev.* B **46** 7707
MacDonald A H 1992 *Solid State Commun.* **84** 109
[6] Hill R N 1977 *Phys. Rev. Lett.* **38** 643; 1977 *J. Math. Phys.* **12** 2316
[7] Bányai L 1989 *Phys. Rev.* B **39** 8022
[8] Bryant G W 1990 *Phys. Rev.* B **41** 1243
[9] Hu Y Z *et al* 1990 *Phys. Rev. Lett.* **64** 1805
[10] Abramowitz M and Stegun I A 1970 *Handbook of Mathematical Functions* (New York: Dover)
[11] Mandray A, Huant S and Etienne B 1992 *Europhys. Lett.* **20** 181
[12] Chandrasekhar S 1944 *Astrophys. J.* **100** 176

[13] Loudon R 1959 *Am. J. Phys.* **27** 649
[14] Bányai L *et al* 1987 *Phys. Rev.* B **36** 6099
[15] Zhu J L *et al* 1992 *Phys. Rev.* B **46** 7546
[16] Avron J, Herbst L and Simon B 1977 *Phys. Rev. Lett.* **39** 1068
Larsen D M 1981 *Phys. Rev.* B **23** 4076