Exchange coupling in semiconductor nanostructures:
Validity and limitations of the Heitler-London approach

M.J. Calderón, Belita Koiller, and S. Das Sarma

1Condensed Matter Theory Center, Department of Physics,
University of Maryland, College Park, MD 20742-4111
2Instituto de Física, Universidade Federal do Rio de Janeiro,
Caixa Postal 68528, 21941-972 Rio de Janeiro, Brazil
(Dated: March 23, 2022)

The exchange coupling of the spins of two electrons in double well potentials in a semiconductor background is calculated within the Heitler-London (HL) approximation. Atomic and quantum dot types of confining potentials are considered, and a systematic analysis for the source of inaccuracies in the HL approach is presented. For the strongly confining coulombic atomic potentials in the H₂ molecule, the most dramatic failure occurs at very large interatomic distances, where HL predicts a triplet ground state, both in 3D and in 2D, coming from the absence of electron-electron correlation effects in this approach. For a 2D double well potential, failures are identified at relatively smaller interdot distances, and may be attributed to the less confining nature of the potential, leading to larger overlap. We find that in the double dot case, the range of validity of HL is improved (restricted) in a related 3D (1D) model, and that results always tend to become more reliable as the interdot distance increases. Our analysis of the exchange coupling is of relevance to the exchange gate quantum computer architectures in semiconductors.

PACS numbers: 03.67.Lx, 85.35.Be, 73.21.La, 85.30.-z

I. INTRODUCTION

Semiconductor spin-based quantum computation emerged from theoretical proposals showing that the required universal gate could be implemented through physical operations involving single electrons bound to an array of quantum dots or to donors. The localized spin of each electron serves as the single qubit by virtue of the 2-level spin-dynamics, and the (electrostatic) quantum mechanical exchange coupling between the two electrons can be used to entangle the qubits through the “exchange gate”.

Accurate calculations of exchange coupling in molecules (or artificial molecules) are extremely difficult requiring numerically intensive self-consistent solutions of Hartree-Fock equations. In semiconductor nanostructures, particularly in the context of quantum computer architectures, such intensive quantum chemistry-type numerical calculations are unwarranted for several reasons. First, the parameters entering such calculations are essentially only very approximately known in semiconductor nanostructures and, therefore, extremely accurate quantitative calculations for the exchange energy in these nanostructures is not particularly meaningful. Second, the quantum chemical type exchange calculations are not particularly valid in the semiconductor environment.

One of the simplest and most successful methods for the calculation of exchange coupling in small molecules was proposed in 1927 by Heitler and London. The basic assumption of the Heitler-London (HL) method is that the many-electron lowest energy wavefunctions in molecules may be written in terms of the one-electron ground-state orbitals of the isolated constituent atoms.

This immediately requires that the overlap (S) among neighboring orbitals be small, a condition not always fulfilled in real molecules. In fact, for the equilibrium interatomic distance in the H₂ molecule (1.5 a₀, with a₀ representing the Bohr radius), the overlap is larger than 0.7, and the HL ground-state energy is overestimated by 5 eV, while for interatomic distances R > 5 a₀ the overlap becomes smaller than 0.1 and an excellent agreement is obtained between HL and the experimentally observed ground-state energy. The HL approximation is thus expected to be valid for S < 1, or equivalently, for well separated atoms.

A somewhat surprising anomaly of the HL method applied to H₂ is that it predicts a triplet ground-state for R > 50 a₀, in contradiction with the well established result that, for a spin-independent Hamiltonian and in the absence of magnetic fields, the ground-state of an even-electron system in a symmetric potential must be a singlet. This anomaly in HL comes from the singular nature of the Coulomb potential leading to a logarithmic dependence of the electron-electron repulsion energy with R which becomes the dominant term at large R, resulting in a negative value of the exchange coupling J(R) = E_{triplet} - E_{singlet} in this limit. An asymptotically correct expression for J(R) for the hydrogen molecule was obtained by Herring and Flicker who have also shown that the HL results for J(R) are in excellent quantitative agreement with the asymptotic expression up to R values very near the crossover to the unphysical negative range of J(R).

Many calculations of exchange coupling in semiconductor quantum dots are based in the HL approximation applied to 2D model potentials. It has been pointed out that, for some parameter values of a quartic model po-
tial proposed for the study of 2D double quantum dots, unphysical (negative) values of $J$ are obtained within the HL approximation. This failure of HL may be due to the reduced dimensionality of the potential, since the electron-electron Coulomb interaction in 2D is expected to be larger than in 3D, or to some intrinsic limitation of this approach when applied to weakly confining gated potentials as compared to atomic-like molecular potentials. We address these questions here by considering the 2D hydrogen molecule and the two-electron double quantum dot quartic potential within HL, including its modified versions in 3D and 1D.

Our study is complementary to detailed and numerically intensive calculations of exchange. We find that the reliability of HL depends primarily on the form of the confining potential: (i) For weakly confining (low barrier) potentials, the range of validity is generally improved in larger space dimensions; (ii) For strongly confining potentials, illustrated here by the coulombic potential, the space dimensionality is not a decisive parameter; (iii) Unreliable and even unphysical results may be attributed to non-additive model potentials intended to simulate a double-well environment.

This paper is organized as follows: In Sec. II we quickly review the HL method for the $H_2$ molecule, and consider the two-dimensional analogue of this problem; in Sec. III we present the HL solution for the two-electron problem in the 2D double quantum dot quartic potential introduced in Ref. 3 and compare it to its modified versions in 3D and in 1D. Further discussions and conclusions are presented in Sec. IV.

II. THE HL METHOD FOR THE $H_2$ MOLECULE IN 2D AND 3D

The Hamiltonian of the hydrogen molecule with nuclear coordinates $\mathbf{R}_A$ and $\mathbf{R}_B$ is written as

$$H = T_1 + T_2 + V(r_1) + V(r_2) + \frac{e^2}{r_{12}} + \frac{e^2}{R},$$

where $V(r_i) = V_A(r_i) + V_B(r_i) = -\frac{e^2}{r_{ia}} - \frac{e^2}{r_{ib}}$, $r_{ia} = |\mathbf{r}_i - \mathbf{R}_A|$, $r_{ib} = |\mathbf{r}_i - \mathbf{R}_B|$, $\mathbf{r}_i$ ($i = 1, 2$) are the electronic coordinates, $T_i$ is the kinetic energy operator for electron $i$, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and $R = |\mathbf{R}_A - \mathbf{R}_B|$ is the inter-nuclear separation. Starting from normalized hydrogen atomic orbitals centered at $\mathbf{R}_A$ and $\mathbf{R}_B$, which we denote for each electron $i$ as $a(i)$ and $b(i)$, the HL lowest singlet (+) and triplet (−) 2-electron states (we omit the spin-dependent part here) are written as

$$|\pm\rangle = \frac{1}{\sqrt{2(1 \pm S^2)}}[a(1)b(2) \pm b(1)a(2)],$$

with $S = \langle a(i)|b(i)\rangle$ giving the overlap integral. It is convenient to cast the exchange coupling, $J = E_{\text{triplet}} - E_{\text{singlet}} \equiv \langle -|H| - \langle +|H| + \rangle$ in the following form

$$J = \frac{2S^2}{1 - S^4}(W - C)$$

where

$$W = \langle a(1)b(2)|v|a(1)b(2) - \frac{1}{S^2}\langle a(2)b(1)\rangle$$

with $v = V(r_1) + V(r_2) - V_B(r_2) - V_A(r_1)$, and

$$C = \langle a(1)b(2)|\frac{e^2}{r_{12}}| - a(1)b(2) + \frac{1}{S^2}\langle a(2)b(1)\rangle.$$
critical $R$ at which $J$ becomes negative is between 40 and 100$\alpha_B$, comparable to the 3D value. At very short
distances, $\mathrm{HL}$ becomes less reliable due to the large overlap [see Fig. 4(a)]. Arbitrarily defining a cutoff at $S = 0.1$,
we estimate the minimum distance at which we can trust the $\mathrm{HL}$ results to be $R_{\min} \sim 5\alpha_B$, and $R_{\min} \sim 2.5\alpha_B$, since the overlap for the 2D system decays much faster with $R$ than for 3D.

III. THE $\mathrm{HL}$ METHOD FOR THE QUARTIC
DOUBLE-DOT POTENTIAL

Quantum dots are defined by gate-generated potentials modifying a two-dimensional electron gas (2DEG) environment in semiconductor heterostructures. Each quantum dot is usually modeled by a harmonic well with $V_j(r) = \frac{m\omega^2_j}{2}(r - R_j)^2$ where $R_j = +R/2 \hat{x}$, $-R/2 \hat{x}$ for $j = A, B$ respectively. Following Burkard et al., the coupling of the dots in a 2D system is modeled by the quartic potential

$$V(x, y) = \frac{m\omega^2}{2} \left\{ \frac{x^2 - (R/2)^2}{R^2} + y^2 \right\}$$

which satisfies $V(x \approx \pm R/2, y) = V_j(r)$. Note that the barrier height increases with $R$. The Hamiltonian for two electrons in a double quantum dot can be written as

$$H = T_1 + T_2 + V(r_1) + V(r_2) + \frac{e^2}{\epsilon r_{12}}$$

where $\epsilon$ is the semiconductor dielectric constant. For the results presented below, distances are given in units of $a^* = \hbar^2/(m^* e^2)$ and energies in $\text{Ry} = m^* e^2/(2\hbar^2 c^2)$, where $m^*$ is the effective mass in the host semiconductor. Note that, contrary to the $H_2$ case, $V \neq V_A + V_B$. The single electron Hamiltonian is

$$h_i = T_i + V_A(r_i),$$

the corresponding ground state orbital is $\phi_{2D}(i) = \frac{\beta}{\sqrt{\pi}} \exp \left\{ -\frac{\beta^2}{2} \left( x_1 \pm \frac{R}{2} \right)^2 + y_i^2 \right\}$, with $\beta = \sqrt{m^* \omega_0/\hbar}$, and the overlap is given by $S_{2D} = \exp(-\beta^2 (R/2)^2)$.

We point out that the physical significance of the covalent term $W$ defined in Eq. 4 is somewhat different here as compared to the $H_2$ system. From Eq. 4, the operator involved in $W$ is an effective potential $v = V(r_1) + V(r_2) - V_B(r_2) - V_A(r_1)$ which, for $H_2$, results in $v = V_B(r_1) + V_A(r_2)$, related to the energy of an “$A$-atom electron” due to the potential $V_B$ of the $B$-atom and vice versa. In the double quantum dot, $v \neq V_B(r_1) + V_A(r_2)$, instead the effective potential $v$ involves differences between the quartic potential and quadratic terms. In this way, the “electron in the $A$-dot” does not “feel” the potential $V_B$, but an approximated version of it.

Using the expressions for $W$ and $C$ given in Eqs. 4 and 5 we get

$$W_{2D} = \frac{3}{4} \hbar \omega_0 \left( 1 + \frac{\beta^2 R^2}{4} \right),$$

and

$$C_{2D} = \hbar \omega_0 \left[ 1 - e^{-\frac{\beta^2\hbar^2}{4} I_0 \left( \frac{\beta^2 R^2}{4} \right)} \right]$$

where $I_0$ is the modified Bessel function of the first kind and

$$c = \sqrt{\frac{\pi}{2}} \frac{e^2 \beta/\epsilon}{\hbar \omega_0}$$

is a parameter introduced in Ref. 3 as the ratio between the Coulomb and the confining energy. Note that $c$ is also completely defined by $\omega_0$, since $\beta \sim \sqrt{\omega_0}$.

In order to investigate the effect of dimensionality, it is instructive to compare the 2D system with a similar 3D problem. From the 2D potential in Eq. 6, we define a 3D counterpart $V_{3D}(x, y, z) = V(x, y) + \frac{m\omega^2}{2} z^2$, with the ground state orbital $a_{3D}(i) = \frac{\beta}{\sqrt{\pi}} \exp \left\{ -\frac{\beta^2}{2} \left( x_1 \pm \frac{R}{2} \right)^2 + y_i^2 + z_i^2 \right\}/2$, leading to $S_{3D} = S_{2D}$, $W_{3D} = W_{2D}$ and

$$C_{3D} = \frac{2}{\sqrt{\pi}} \hbar \omega_0 c \left[ 1 - \sqrt{\frac{1}{2}} \text{Erf}(\beta R/\sqrt{2}) \right],$$

where $\text{Erf}$ is the error function.
where \( \text{Erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du \) is the Error Function.

For completeness, we also discuss the 1D problem. The model potential is \( V_1D(x) = \frac{m \omega_0^2}{2} \left[ x^2 - \left( \frac{R}{2} \right)^2 \right]^2 / R^2 \). The single-electron ground state is \( a_{1D}(i) = \sqrt{\frac{2}{\pi \hbar}} \exp \left\{ -\beta^2 \left[ x_i \pm \frac{R}{2} \right]^2 / 2 \right\} \), leading to \( S_{1D} = S_{2D}, W_{1D} = W_{2D} \). The Coulomb term corresponds to the \( \varepsilon = 0 \) value of the function

\[
C_{1D}(\varepsilon) = \frac{2}{\pi} \hbar \omega_0 c \int_0^\infty dx \frac{e^{-\beta^2 x^2/2}}{x} - \frac{2}{\pi} \hbar \omega_0 c S^2 \int_0^\infty dx \frac{e^{-\beta^2 x^2/2}}{x} \cosh(\beta^2 R x),
\]

where \( x = |x_1 - x_2| \). In the \( \varepsilon \to 0 \) limit, the singular nature of the Coulomb potential in 1D systems leads to a logarithmic divergence of this expression. We overcome this problem phenomenologically by introducing a cutoff distance (the results presented in Fig. 2 correspond to \( \varepsilon = 0.2a^* \)) to simulate the correlation effects that would lead to a lower probability density at \( x_1 = x_2 \). Such correlation effects are not included in HL.

Fig. 2 shows the behavior of \( S, W, C \) vs \( R \) for different values of \( c \) and dimensionalities. The HL approach breaks down for small \( R \) for a certain value of \( c \) which depends on dimensionality. For 2D, the breakdown occurs when \( c > 2.8 \), as mentioned by Burkard et al.\(^{22}\) Meanwhile, for 3D HL fails for \( c > 5.8 \), and for \( c > 1.95 \) for 1D.\(^{21}\) On the other hand, at large enough \( R \) one always gets \( W > C \) and thus positive \( J \), regardless of \( c \). Hence, the large-\( R \) anomaly encountered in the H\(_2\) HL solution does not occur here. We may argue that the large-\( c \) failure of the HL approximation is ultimately due to a large-\( S \) regime [see Fig. 4(a)].

The exchange calculated from Eq. (43) for the 2D system is given in Fig. 3(a) for the same values of \( c \) as in Fig. 2. Note that for the largest \( c \) values the curves are interrupted when \( J \) becomes negative, and for \( R \) just above this point HL predicts the equally unphysical behavior of \( J \) increasing with \( R \).\(^{22}\) For \( c = 2.1 \), \( J \) decreases monotonically with \( R \), but the “shoulder” at \( R \approx 4a^* \) is a precursor signaling this anomaly, meaning that \( J > 0 \) is not a sufficient condition for the reliability of the HL results. For distances far beyond these anomalous points, we find that the general behavior of \( J(R) \) is dominated by the \( S^2 \) prefactor in Eq. (43), as shown in the inset to Fig. 3(a).

From a formal point of view, it would be interesting to present a direct comparison of the \( R \to \infty \) behavior of \( J(R) \) calculated within HL with asymptotic expressions such as given in Fig. 1(c) for \( \text{H}_2 \), obtained through the so-called median-plane method. This method was originally introduced for two hydrogen atoms\(^{21}\) and has been extended to a variety of problems in atomic and semiconductor physics. However, it is not directly applicable to the potential in Eq. (43) because, in the asymptotic limit, this model potential displays an essentially infinite barrier between the dots.\(^{22}\) We present instead a qualitative comparison of our results in Fig. 3(a) with those obtained from an interpolated formula for the exchange coupling of two electrons under a potential related to ours,\(^{22}\) namely the potential created by donor impurities close to a 2DEG. The connection between our results and those in Ref. 18 is based on the fact that when a single impurity is far from the 2DEG, the electronic potential it creates may be approximated by a parabolic confinement, whose curvature defines \( \omega_0 \) and thus \( c \). The results plotted in Fig. 3(b) are obtained from Eq. (44) in Ref. 18 for distances between the donor and the 2DEG \( h = 2, 4 \), and 10\( a^* \), resulting in \( c = 2.1, 3.5 \), and 7 respectively. We note that the general trends in Figs. 3(a) and (b) are the same, though a detailed quantitative agreement is not found. This lack of agreement is due to the different nature of the barrier between the parabolic potentials. As noted above, the exchange energy within HL scales asymptotically as \( S^2 \), thus for the quartic model the exchange has an exponential decay with \( R^2 \), while for the impurity potential in Ref. 18 the two-electron wave-functions, and consequently \( S \) and \( J \), have a slower exponential decay with \( R \).

We conclude that HL is essentially reliable, at least qualitatively, for the double quantum dot problem at large enough interdot separations. In the large over-
lap region, HL is not applicable regardless of the sign of $J$. We have attempted a standard improvement to HL, which for the $H_2$ problem is to consider the Bohr radius as a variational parameter. In the present case this consists in taking $\beta$ as a variational parameter. Although we obtain some lowering of the singlet and triplet energies by this procedure, no qualitative improvement is obtained. Another straightforward improvement is the Hund-Mulliken approach, in which the double occupancy states $a(1)a(2)$ and $b(1)b(2)$ are included in the basis set for the 2-electron states. This method lowers the singlet energy with respect to the triplet, but the failure at large $c$ remains.

**IV. SUMMARY AND CONCLUSIONS**

In this work, we have analyzed the reliability of HL for two types of “double-well” potentials where the individual-well confinement potentials are of different natures: Atomic (Hydrogen atom) in Sec. III or harmonic (quantum dot) in Sec. IV. There are two main differences between these problems: One refers to the strength of the confinement, much stronger in the first case, and the other to their dimensionality, 3D for atoms and 2D for quantum dots defined over a 2DEG.

For the 3D $H_2$ case, it has been long known that HL fails, namely, the triplet state is predicted to become the ground-state, when the atoms are very far apart ($R \sim 50a_B$). As argued above, at short distances HL is expected to fail as well, and it does as it overestimates the ground-state energy. We have also considered the 2D hydrogenic molecule within HL, and found qualitatively the same behavior and limitations as for the 3D $H_2$ case, meaning that the strongly confining atomic potential is the dominant aspect of this problem both in 3D and in 2D.

Our study of the particular quartic potential proposed by Burkard et al. for modeling coupled harmonic dots shows that the failure of HL at short distances is more dramatic here than in $H_2$ due to the less confining potential, leading to larger overlap: A triplet ground-state is predicted for a wide range of parameters. We have also pointed out the fact that the quartic potential is not additive (i.e. it does not correspond to the superposition of the isolated harmonic potentials) as another possible source for this failure. Overcoming these limitations for the exchange calculation, in particular when the overlap is large, requires going beyond the HL approximation, for example increasing the basis set for the two- or many-electron wave-functions to incorporate a set of excited one-electron states. Different methods have been adopted in the literature: Molecular orbital, configuration-interaction, exact diagonalization, and unrestricted Hartree-Fock.

Molecular orbital calculation of double-dot model potentials have been explicitly compared to HL, and in all cases an excellent qualitative agreement is obtained. According to the model potential, practically complete agreement may be obtained while deviations of up to 50\% have also been reported. Also, spin polarized DFT calculations can be done to obtain the exchange energy but it is difficult to estimate the reliability of such theories in the present scenario. Unfortunately none of the cited methods has the conceptual and computational simplicity of HL, which, coupled to a careful choice for the model potential, should be always attempted as a first approximation for estimating exchange coupling in new systems.

**Acknowledgments**

We thank Pavel Krotkov for useful discussions. This work is supported by LPS and NSA. BK also acknowledges support by CNPq, FUJB, Millenium Institute-CNPq, and FAPERJ.
This is the case for the particular cutoff considered ($\varepsilon = 0.2a^*$). The smaller the cutoff parameter $\varepsilon$, the larger the value of $C_{1D}$, and the lower the value of $c$ that will cause $H_L$ to give a negative exchange. Strictly speaking, $H_L$ always predicts a triplet ground state for this 1D model, a characteristic that should be expected in 1D systems if electron-electron correlations are not taken into account.

Band interference effects, which are not relevant here, may lead locally to this behavior as obtained in Ref. 29.

The median-plane method consists of reducing the expression for $J$ to a surface integral over a hyperplane in coordinate space, and using a perturbative approach to determine the two-electron wavefunction. The accuracy of the perturbative approach has been demonstrated (see for example Refs. 13 and 16) for additive potentials such that the contribution from each confining center tends to zero at large distances from the location of its minimum.

References:

1. A. Barenco, C. H. Bennett, R. Cleve, D. P. DiVincenzo, N. Margolus, P. Shor, T. Sleator, J. A. Smolin, and H. Weinfurter, Phys. Rev. A 52, 3457 (1995).
2. D. Loss and D. P. DiVincenzo, Phys. Rev. A 57, 120 (1998).
3. G. Burkard, D. Loss, and D. P. DiVincenzo, Phys. Rev. B 59, 2070 (1999).
4. X. Hu and S. Das Sarma, Phys. Rev. A 61, 062301 (2000).
5. R. de Sousa, X. Hu, and S. Das Sarma, Phys. Rev. A 64, 042307 (2001).
6. S. Tarucha, D. G. Austing, T. Honda, R. van de Hage, and L. Kouwenhoven, Phys. Rev. Lett. 77, 3613 (1996).
7. L. Kouwenhoven, T. Oosterkamp, M. Danoesastro, M. Eto, D. G. Austing, T. Honda, and S. Tarucha, Science 278, 1788 (1997).
8. J. R. Petta, A. C. Johnson, J. M. Taylor, E. A. Laird, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Science 309, 2180 (2005).
9. A. C. Johnson, J. R. Petta, J. M. Taylor, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, Nature 435, 925 (2005).
10. J. Gorman, D. G. Hasko, and D. A. Williams, Phys. Rev. Lett. 95, 005052 (2005).
11. B. E. Kane, Nature 393, 133 (1998).
12. W. Heitler and F. London, Z. Physik 44, 455 (1927).
13. C. Herring, Rev. Mod. Phys. 34, 631 (1962).
14. J. C. Slater, Quantum Theory of Molecules and Solids, vol. 1 (McGraw-Hill, New York, 1963).
15. E. Lieb and D. Mattis, Phys. Rev. 125, 164 (1962).
16. C. Herring and M. Flicker, Phys. Rev. 134, A362 (1964).
17. I. Ponomarev, V. Flambaum, and A. L. Efros, Phys. Rev. B 60, 5485 (1999).
18. I. Ponomarev, V. Flambaum, and A. L. Efros, Phys. Rev. B 60, 15848 (1999).
19. V. W. Scarola and S. Das Sarma, Phys. Rev. A 71, 032340 (2005).
20. M. Helle, A. Harju, and R. M. Nieminen, Phys. Rev. B 72, 205329 (2005).
21. C. Yannouleas and U. Landman, Int. J. Quantum Chem. 90, 699 (2002).
22. M. Stopa, A. Vidan, T. Hatano, S. Tarucha, and R. M. Westervelt, cond-mat/0507591 (2005).
23. B. Koiller, X. Hu, and S. Das Sarma, Phys. Rev. Lett. 88, 027903 (2002).