

1. Publication Nº <i>INPE-2981-PRE/443</i>	2. Version	3. Date <i>Dec., 1983</i>	5. Distribution <input type="checkbox"/> Internal <input checked="" type="checkbox"/> External <input type="checkbox"/> Restricted
4. Origin <i>DTE/DCT</i>	Program <i>MATERIALS</i>		
6. Key words - selected by the author(s) <i>TWO-DIMENSIONAL SYSTEM</i> <i>2D MOLECULAR INTEGRALS</i> <i>HYDROGEN MOLECULES</i>			
7. U.D.C.: <i>539.2</i>			
8. Title <i>INPE-2981-PRE/443</i>		10. Nº of pages: <i>10</i>	
<i>THE HYDROGEN MOLECULE FOR A TWO-DIMENSIONAL SYSTEM</i>		11. Last page: <i>8</i>	
9. Authorship <i>A. Ferreira da Silva</i> <i>M. Fabbri</i>		12. Revised by <i>Ram Kishore</i>	
Responsible author <i>A/S.</i>		13. Authorized by <i>Parada</i> <i>Nelson de Jesus Parada</i> <i>Director General</i>	
14. Abstract/Notes <p><i>The two-dimensional (2D) energy of the hydrogen molecule is carried out by the Heitler-London method. The 2D integrals (which are more localized compared to 3D ones) are performed in the light of the 3D Slater integrals. A discussion of such 2D system is briefly outlined for doped semiconductors.</i></p>			
15. Remarks <i>This paper will be submitted to International Journal of Quantum Chemistry.</i>			

THE HYDROGEN MOLECULE FOR A TWO-DIMENSIONAL SYSTEM

A. FERREIRA DA SILVA and M. FABBRI

Instituto de Pesquisas Espaciais - INPE
Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq
12200 São José dos Campos, SP, Brasil

ABSTRACT

The two-dimensional (2D) energy of the hydrogen molecule is carried out by the Heitler-London method. The 2D integrals (which are more localized compared to 3D ones) are performed in the light of the 3D Slater integrals. A discussion of such 2D system is briefly outlined for doped semiconductors.

1. INTRODUCTION

The three-dimensional (3D) Slater integrals [1] have been the subject of a large number of theoretical studies in molecular physics as well as in problems connected to doped semiconductors [2-6]. Due to the random distribution of the impurities in the semiconductors, it is possible to have a pair of impurities very close to each other forming a H₂-type impurity molecule [3-5]. In a doped semiconductor the electron hopping between impurities spreads the impurity levels into impurity bands [4-7]. The energy of the impurity molecule can be calculated analytically in terms of the Slater integrals [1, 4, 5] in a LCAO-type approximation. Besides their intrinsic theoretical interest in 3D systems, they are also of great interest in 2D systems like impurities in inversion layer in MOS (Metal-Oxide-Semiconductor) structures [8]. Such integrals, calculated and shown below, are very sensitive to change in the dimensionality of the system. It is therefore the purpose of the present work to carry out the numerical calculation of the 2D integrals, in the light of the 3D Slater integrals, in order to calculate the energy of the 2D H₂-molecule by the Heitler-London Method.

2. THE 2D HEITLER-LONDON ENERGY

In three dimensions, the energy of a neutral hydrogen atom is -0.5 Hartree and its wave function is (in the Slater notation)

$$a(1) = (1/\pi a_H^3)^{1/2} \exp(-r_{1a}/a_H) , \quad (1)$$

centered around the atom located at \vec{R}_a , where $r_{1a} = |\vec{r}_1 - \vec{R}_a|$, \vec{r}_1 labels the coordinate of the electron and a_H is the effective Bohr radius. In two dimensions, the energy of the hydrogen atom is -2.0 Hartrees and its wave function [8,9] is

$$a(1) = (8/\pi)^{1/2} a_H^{-1} \exp(-2r_{1a}/a_H) . \quad (2)$$

The Heitler-London two-particle wave function for the lowest state of the H₂-molecule [4,5] can be written as

$$\Psi(ab; r_{1a} r_{2b}) = \beta [a(1) b(2) + b(1) a(2)] , \quad (3)$$

where β is the normalization constant. Choosing the units $m = \hbar = e^2/\kappa = 1$, the Hamiltonian is written as

$$H = - \frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,j} |\vec{r}_i - \vec{R}_j|^{-1} + \frac{1}{r_{12}} + \frac{1}{R_{ab}} , \quad (4)$$

where

$$\begin{aligned} i &= 1, 2, & r_{12} &= |\vec{r}_1 - \vec{r}_2| , \\ j &= a, b, & R_{ab} &= |\vec{R}_a - \vec{R}_b|/a_H . \end{aligned}$$

The lowest energy state of the 2D impurity molecule,

$$E = \langle \Psi(ab; r_{1a} r_{2b}) | H | \Psi(ab; r_{1a} r_{2b}) \rangle , \quad (5)$$

can be rewritten in terms of the modified Slater integrals S , K , J , J' and K'

$$E(R_{ab}) = \frac{1}{(1+S^2)} \left[4(J+KS-1) + (J'+K'-S^2) + \frac{1}{2R_{ab}} \right]. \quad (6)$$

The normalization constant is $\beta = [2(1+S^2)]^{-1/2}$, and the integrals evolved in the 2D energy are

$$\langle a(1) | -\nabla_1^2/2 | a(1) \rangle_{2D} = 2, \quad (7)$$

$$\langle a(1) | -1/r_{1a} | a(1) \rangle_{2D} = -4, \quad (8)$$

$$\langle a(1) | b(1) \rangle_{2D} = S = 2R^2 \left[K_0(2R) + \frac{1}{R} K_1(2R) \right], \quad (9)$$

$$\langle a(1) | -1/r_{1b} | b(1) \rangle_{2D} = 2K = -8R K_1(2R), \quad (10)$$

$$\langle a(1) | -\nabla_1^2/2 | b(1) \rangle_{2D} = -(2K+S), \quad (11)$$

$$\langle a(1) | -1/r_{1b} | a(1) \rangle_{2D} = 2J = -4 \left[1 - 4R J_1(2R) K_0(2R) \right], \quad (12)$$

$$\langle a(1) b(2) | 1/r_{12} | b(1) a(2) \rangle = K' = (0.415R + 2.776) S^2. \\ [1 - \exp(-0.85R)] / R, \quad (13)$$

$$\langle a(1) b(2) | 1/r_{12} | a(1) b(2) \rangle = J' = \left[\frac{1}{R} - \left(\frac{1}{R} - 3.1R + 1.1R^2 - 0.3R^2 \right) \exp(-2.36R) \right]. \quad (14)$$

The Coulomb integrals K and J' are commonly called electron hopping energy integral and electron correlation integral, respectively. K' and

S are respectively exchange and overlap integrals. K_0 and K_1 are the modified Bessel functions of zero and first order, respectively. J_1 is Bessel's function of first order and $R = R_{ab}$. We found Eqs. (13) and (14) to be the best fitted analytical curves for K' [10] and J' .

3. DISCUSSION

In Figures 1a and 1b we show the 2D and 3D Slater integrals, respectively. We see that all the 2D integrals are more localized than the 3D Slater integrals. Therefore, the charge density for 2D wave function (Eq. (2)) is more localized, compared to its value for 3D wave function (Eq. (1)) [9]. The energy obtained for the 2D hydrogen molecule is shown in Figure 2, together with the energy for the 3D case [1, 4]. At the equilibrium distance ($R = 0.174$ a.u.) the 2D energy is quoted as -13 Hartrees. For large separation ($R \rightarrow \infty$) the problem reduces to two isolated 2D hydrogen atoms (-4.0 Hartrees). For comparison, in 3D, at the equilibrium distance, $R = 1.12$ a.u., the energy is -1.115 Hartrees and for $R \rightarrow \infty$ the energy is -1.0 Hartree. Recently, by taking into account only the hopping and overlap integrals, Ferreira da Silva and Fabbri [9] have shown that 2D impurity density of states is drastically different compared to 3D one. The complete calculation for 2D impurity density of states, by including all the 2D Slater integrals, is the subject of our next work. We hope to report it soon.

BIBLIOGRAPHY

- [1] J.C. Slater, Quantum Theory of Molecules and Solids, Vol. 1 (McGraw-Hill, New York, 1963), chaps. 3 and 4; Quantum Theory of Matter, 2nd ed. (McGraw-Hill, New York, 1968), chap. 21.
- [2] K.-F. Berggren, Phil. Mag. 27, 1027 (1973).
- [3] N.-I. Franzén and K.-F. Berggren, Phil. Mag. B43, 29 (1981).
- [4] A. Ferreira da Silva, M. Fabbri and I.C. da Cunha Lima, Phys. Status Solidi B115, 311 (1983).
- [5] K.A. Chao and A. Ferreira da Silva, Int. J. Quantum Chem.: Quantum Chem. Sym. 12, 461 (1978).
- [6] M. Fabbri and A. Ferreira da Silva, J. Non-Cryst. Solids 55, 103 (1983); R. Riklund, A. Ferreira da Silva and K.A. Chao, Phil. Mag. B42, 755 (1980).
- [7] H. Kamimura, The Metal Non-Metal Transition in Disordered Systems, eds. L.R. Friedman and D.P. Tunstall (Univ. of Edinburgh, SUSSP Publications, 1978); A. Ferreira da Silva, R. Kishore and I.C. da Cunha Lima, Phys. Rev. B23, 4035 (1981).
- [8] F. Stern and W.E. Howard, Phys. Rev. 163, 816 (1967); I.C. da Cunha Lima, A. Ferreira da Silva and M. Fabbri, Surface Sci. 135 (1983) (in press).
- [9] A. Ferreira da Silva and M. Fabbri, J. Phys. C: Solid St. Phys. (to be published).
- [10] M. Fabbri and L.F. Perondi, Int. J. Quantum Chem. (submitted).

FIGURE CAPTIONS

Fig. 1 - The molecular integrals in two (a) and three (b) dimensions.

Fig. 2 - Energies of hydrogen molecule, as determined by Hitler-London method, for two- and three-dimensional (2D and 3D) cases. The arrow indicates the equilibrium distance. The 2D energy scale is divided by 10.

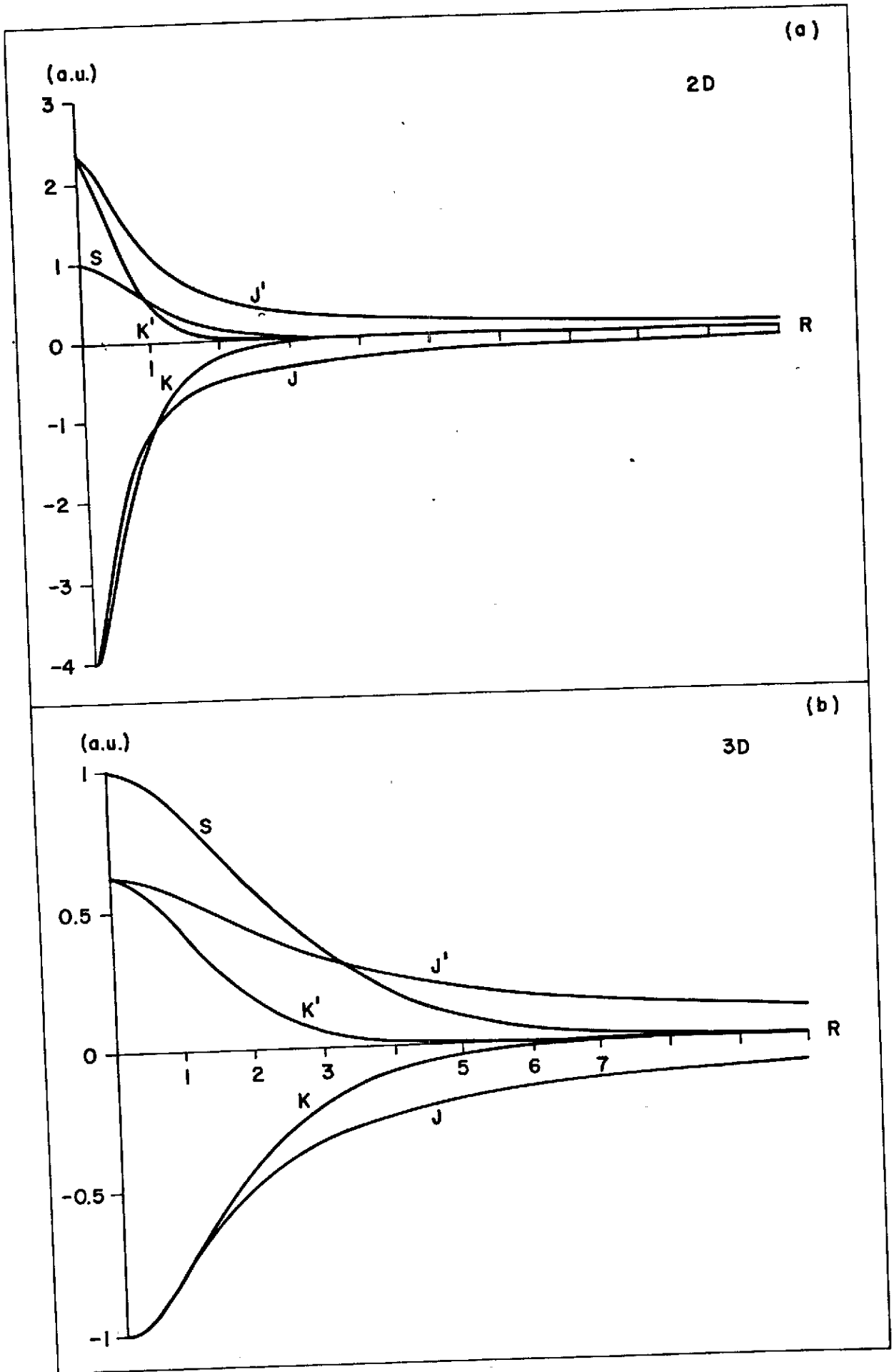


Fig. 1 - A. Ferreira da Silva and M. Fabbri

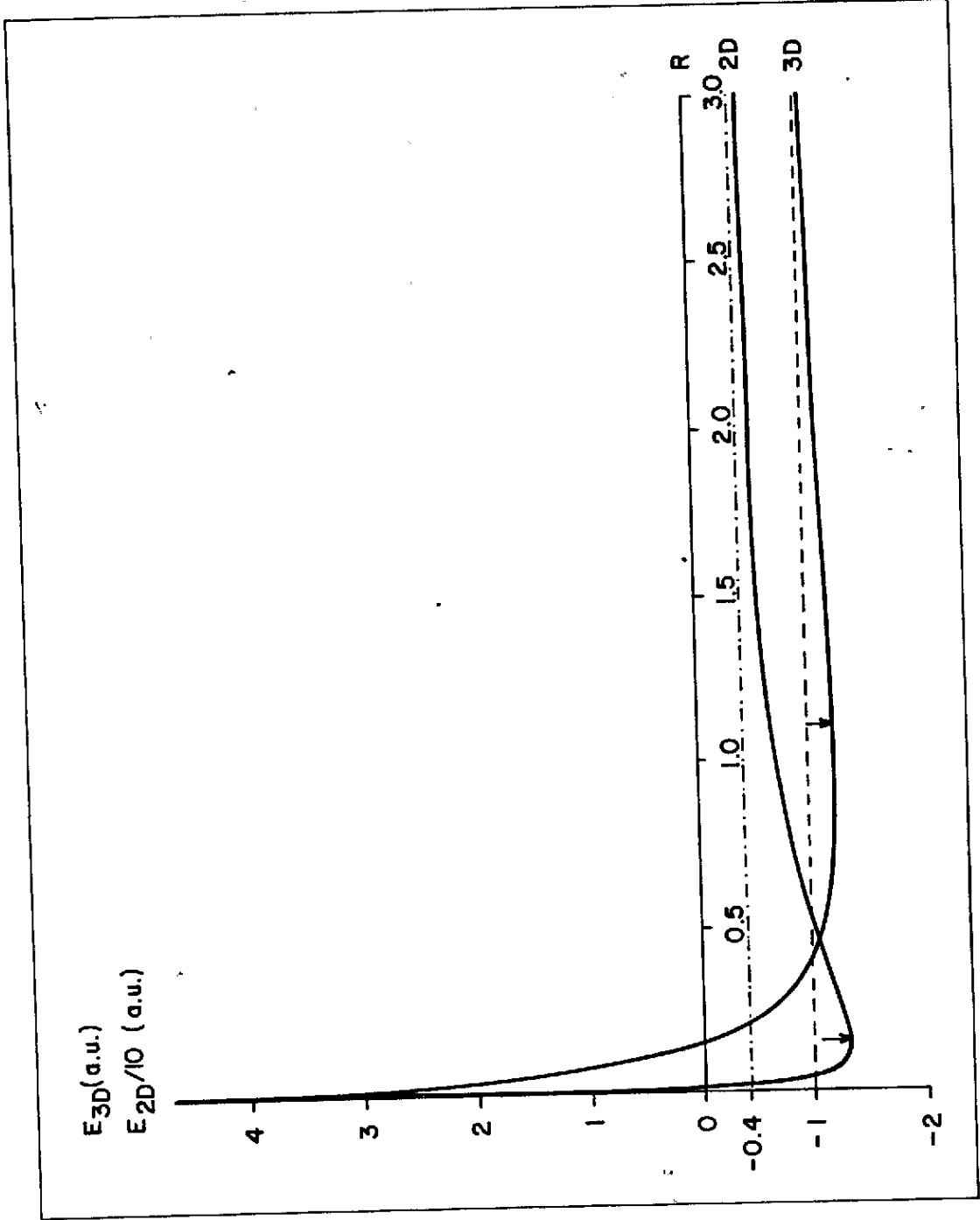


Fig. 2 - A. Ferreira da Silva and M. Fabbri