Two-dimensional hydrogen molecule and the alternant-molecular-orbital approximation

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The eigenenergies of the hydrogen molecule are calculated in the alternant-molecular-orbital approximation. Emphasis is given to two-dimensional (2D) systems. Results for the 2D and 3D cases are compared and also with the singlet state of the variational Heitler-London approximation. Unlike what is observed in 3D, in 2D we found that in the ground-state electrons are highly correlated and that double occupancy is inhibited.

In this brief report we present our calculation of the energy levels of a two-dimensional (2D) hydrogen molecule, considering the nuclei to be separated by a distance R. We assume the alternant-molecular-orbital (AMO) approximation,[1] which is briefly described in what follows.

We start with a Hamilitonian:

$$H = H^{\mathrm{el}} + 2/R \ , \tag{1}$$

$$H^{\mathrm{el}} = -\nabla_1^2 - \nabla_2^2 - \frac{2}{r_{1a}} - \frac{2}{r_{1b}} - \frac{2}{r_{2a}} - \frac{2}{r_{2b}} + \frac{2}{r_{12}} \ . \tag{1a}$$

It describes the motion of two interacting electrons in the field of two positive charges, fixed at position a and b, separated by a distance R. H^{el} refers to the electron system. We have used atomic units where the energy is given in rydbergs.

We search for eigenstates corresponding to combinations of 1-s hydrogenlike wave functions and unpaired spins (singlet state), namely,

$$\psi^{\mathrm{AMO}}(\mathbf{r}_1,\mathbf{r}_2) = f_{1\Psi 1}(\mathbf{r}_1,\mathbf{r}_2) + f_{2\Psi 2}(\mathbf{r}_1,\mathbf{r}_2) + f_{3\Psi 3}(\mathbf{r}_1,\mathbf{r}_2) \ , \tag{2}$$

$$\psi_1(\mathbf{r}_1,\mathbf{r}_2) = \phi_a^{1s}(r_1)\phi_b^{1s}(r_2) + \phi_a^{1s}(r_2)\phi_b^{1s}(r_1) \ , \tag{2a}$$

$$\psi_2(\mathbf{r}_1,\mathbf{r}_2) = \phi_a^{1s}(r_1)\phi_a^{1s}(r_2) \ , \tag{2b}$$

$$\psi_3(\mathbf{r}_1,\mathbf{r}_2) = \phi_b^{1s}(r_1)\phi_b^{1s}(r_2) \ . \tag{2c}$$

The solution obtained by assuming $f_2 = f_3 = 0$ is known as the Heitler-London (HL) approximation.

We solve the Schrödinger equation variationally taking for the 2D $\phi^{1s}(r)$ (from now on we will omit the superscript $1s$):

$$\phi(r) = \left[\frac{8}{\pi}\right]^{1/2} \alpha e^{-2\alpha r} \ , \tag{3}$$

where r is a dimensionless distance (in units of the Bohr radius) and α is to be obtained by minimizing the ground energy.[2]

Diagonalizing the above Hamiltonian we obtain the following energy eigenvalues in terms of the overlap S and the matrix elements H:

$$E_{\pm} = \frac{B \pm \sqrt{B^2 - 4AC}}{2A} + \frac{2}{R} \ , \tag{4}$$

where

$$A = 2(1-S^2)^2 \ , \tag{5}$$

$$B = (1+S^2)[H_{11} + 2(H_{22} - H_{23})] - 8SH_{12} \ , \tag{6}$$

$$C = H_{11}(H_{22} + H_{23}) - 2H_{12}^2 \ , \tag{7}$$

and

$$E_1 = (H_{22} - H_{23})/(S_{22} - S_{23}) + \frac{2}{R} \ . \tag{8}$$

The matrix elements H_{ij}, S_{ij} and S are defined by

$$H_{ij} = \langle \psi_i \mid H^{\mathrm{el}} \mid \psi_j \rangle \ , \tag{9}$$

$$S_{ij} = \langle \psi_i \mid \psi_j \rangle \ , \tag{10}$$

$$S = \int d^2 r_1 \int d^2 r_2 \phi(\mid \mathbf{r}_1 - \mathbf{R} \mid)\phi(r_2) \ . \tag{11}$$

Next we express the relevant matrix elements in terms of Slater's integrals:[3]

$$H_{22} = 8\alpha^2 + 2\alpha J - 16\alpha + U \ , \tag{12}$$

$$H_{23} = -2\alpha^2 S(K + 4S) + 4\alpha SK + \alpha K' \ , \tag{13}$$

$$H_{11} = 4\alpha^2(4 - KS - 4S^2) + 2\alpha(J' - 16 + 2J + 4SK + K') \ , \tag{14}$$

$$H_{12} = -2\alpha^2 K + 2\alpha(L + 2K + SJ - 8S) \ , \tag{15}$$

$$S_{11} = 2(1-S^2) \ , \tag{16}$$

$$S_{12} = 2S \ , \tag{17}$$

$$S_{22} = 1 \ , \tag{18}$$

$$S_{23} = S^2 \ . \tag{19}$$

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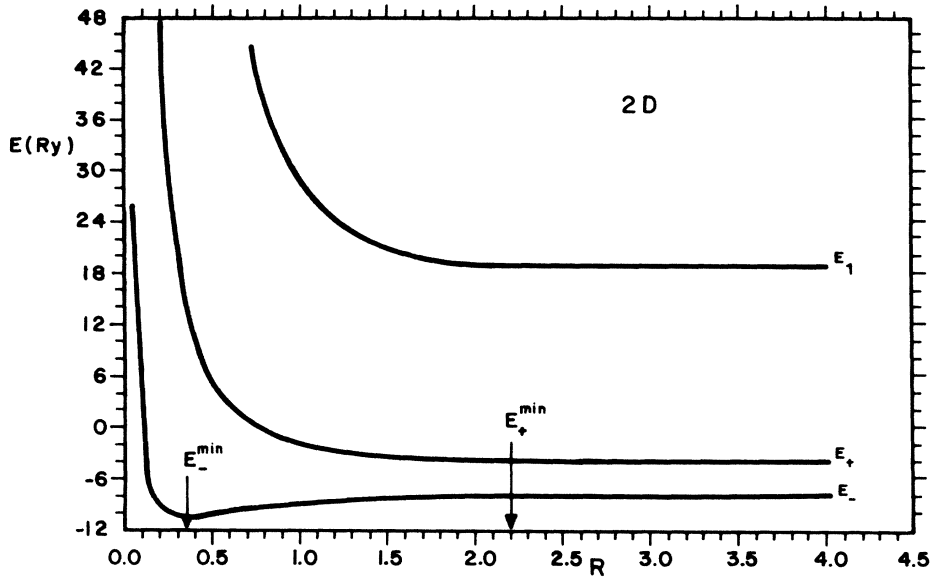

FIG. 1. Calculated eigenenergies of the 2D hydrogen molecule as a function of R. $E_{\pm}^{min}$ is the energy at equilibrium.

The intraatomic correlation energy, U, is equal to 4.71α.[4] The integrals J, S, K, U, K', J', and L that appear here differ from conventional Slater's integrals because they are calculated for the 2D case and depend on the variational parameter α. Their expressions in this case are

$$J=-8[1-4\alpha R I_1(2\alpha R)K_0(2\alpha R)]\,, \tag{20}$$

$$S=2\alpha R\,[K_1(2\alpha R)+\alpha R K_0(2\alpha R)]\,, \tag{21}$$

$$K=-16\alpha R K_1(2\alpha R)\,. \tag{22}$$

The other integrals are obtained by numerical fitting:[5]

$$K'=2(0.415\alpha R+2.776)S^2[1-\exp(-0.85\alpha R)]/\alpha R\,, \tag{23}$$

$$L=2.36[\theta(\alpha R-1.1)\exp(-1.72\alpha R+0.78) +\theta(1.1-\alpha R)\exp(-0.65\alpha^2R^2-0.3\alpha R)]\,, \tag{24}$$

$$J'=1/\alpha R-\exp(-2.36\alpha R)[1/\alpha R-3.1\alpha R +1.1(\alpha R)^2-0,3(\alpha R)^3]\,, \tag{25}$$

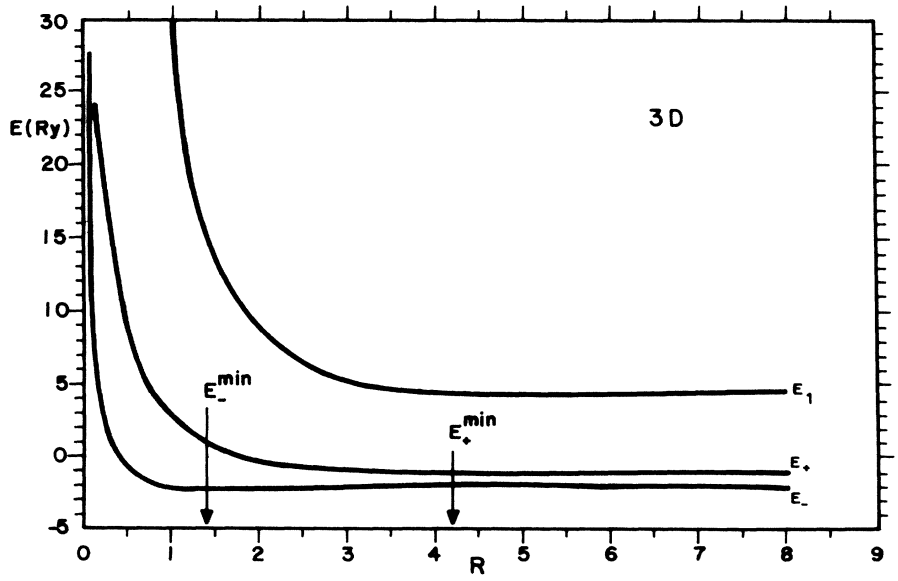

FIG. 2. Calculated eigenenergies of the 3D hydrogen molecule as a function of R. The arrow indicates the equilibrium distance, where E_- is a minimum.

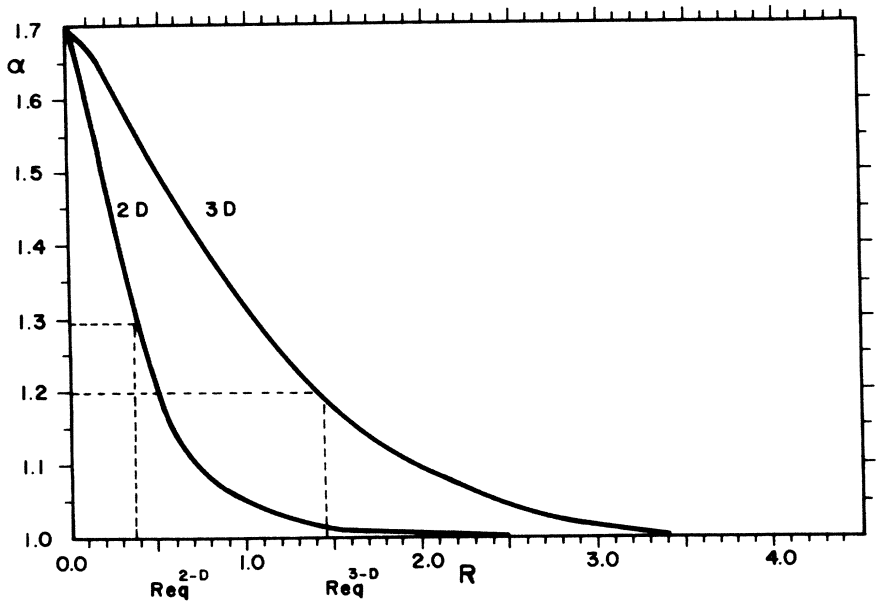

FIG. 3. Variational parameter α for the 3D and 2D hydrogen molecule. For each value of R the curve gives the α that minimizes E_-. The dashed lines indicate the equilibrium values of α and R.

where I_1 is the Bessel function of first order and K_0 and K_1 are the modified Bessel function of zero and first order, respectively. The integrals L, U, and J' represent the electron-correlation, S the overlap, K and electron-hopping energy, and K' the exchange.

For each value of R we have minimized the ground-state energy E_- and, with that particular value of α, obtained E_+ and E_1. The results are shown in Fig. 1. The equilibrium distance is obtained to be $R_{eq}=0.36$, corresponding to $\alpha_{eq}=1.29$ and $E_-=-10.5$ Ry, in good agreement with the HL results.[5] For the sake of comparison, these values for the 3D case are $\alpha_{eq}=1.17$, $R_{eq}=1.41$, and $E_-=-2.28$ Ry for HL and $\alpha_{eq}=1.19$, $R_{eq}=1.43$, and $E_-=-2.296$ Ry for AMO. Figure 2 shows the eigenenergies for the 3D case. Figure 3 shows the variational parameter α as a function of R for two and three dimensions. It is important to observe that the variational AMO introduces in 2D a minimum of -4.08 Ry in E_+ at $R=2.20$, besides that of E_-; in 3D the minimum of E_+ is -1.14 Ry at $R=4.20$.

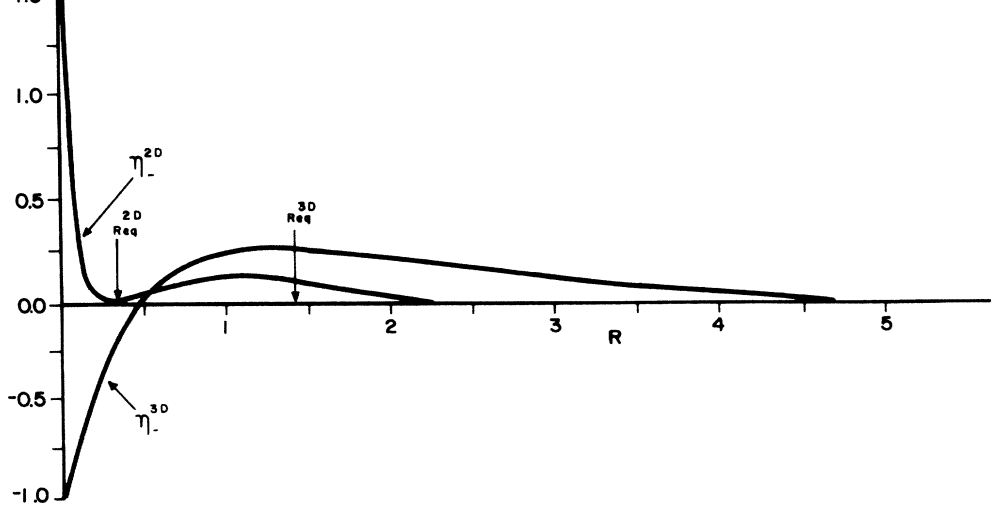

FIG. 4. Rate $\eta=f_2/f_1$ for the ground state E_- as a function of R (details in the text).

The wave function ψ_1 is generally called the covalent component, to distinguish from the ionic components ψ_2 and ψ_3. These terms are really not convenient, as pointed out by Goscinski and Calais,[6] mainly for short distances R. It is important to mention that, even the smallest deviation of R from zero breaks the spherical (circular) symmetry in such a way that f_2/f_1 does not approach the value one for small R, as was pointed out by Chao, Oliveira, Cerqueira, and Majilis[7] in the 3D case.

Defining

$$X=H_{11}-E_-S_{11}\ ,$$

$$Y=H_{12}-E_-S_{12}\ ,$$

we have $\eta_-=X/2Y$. Figure 4 shows η_- as a function of R. We can see that η_-^{2D} is practically zero near the equilibrium distance, differently of η_-^{3D}, which is near a maximum, and then shows some ionicity in the equilibrium configuration. Both η_-^{3D} and η_-^{2D} fall off at large R, as expected. Since η_- measures the double occupancy, we conclude that intrasite correlation is strong enough in 2D, near the equilibrium, to inhibit two electrons to be bound to the same nucleus.

For large separation ($R\rightarrow\infty$) both problems reduce to $\alpha=1$ and $\eta_-=0$ (isolated hydrogen atoms) and the energies of the systems are $E_-^{3D}=-2.0$ Ry and $E_-^{2D}=-8.0$ Ry, respectively. For the first excited state they are $E_+^{3D}=-0.945$ Ry and $E_+^{2D}=-3.9833$ Ry, corresponding to the ground-state energies of a H^- in three and two dimensions in this approximation.

The results shown here can be used to study the formation of hydrogenic bound states associated with impurities in the proximity of inversion layers in semiconductors. These applications are presently in progress.

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