

Variational calculation of the two-dimensional H₂ molecule

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The ground-state energy of the two-dimensional (2D) hydrogen molecule has been calculated using a Heitler-London-Rosen-type variational calculation. The value of the dissociation energy is found to be 2.5 Ry. For the interatomic distance $R=0$, the variational parameter $\alpha^{2D}=1.7055$, corresponding to a 2D He atom. For the sake of comparison, the results of the 3D case are also recalculated. Special interest arises from the Slater integrals, which are rather difficult to obtain in the 2D case.

The problem of the hydrogen molecule has given rise to considerable interest in a large number of theoretical studies, mainly to obtain the best ground-state energy. Many of these studies use the well-known three-dimensional (3D) Slater integrals;¹ such integrals take into account in an explicit way some features of the electron-correlation effects. Besides the intrinsic interest of the H₂ molecule in molecular physics, as well as in doped semiconductors² (in this case forming a H₂-like impurity molecule), it is also a subject of investigation in problems connected to two-dimensional (2D) systems, like impurities in inversion layer in metal-oxide-semiconductor (MOS) structures.³ The change in the dimensionality of such systems leads to the very poorly understood nature of the electronic states in the 2D systems.⁴ In this context, a natural interest arises in doing some of the traditional computations of the 3D molecular systems for their 2D counterparts. We report here, briefly, the results of a Heitler-London-Rosen-type^{1,5} calculation for the ground-state energy of the 2D H₂ molecule.

The Hamiltonian for the H₂ molecule is taken to have the form

$$H = -\sum_i \nabla_i^2 - \sum_{ij} \frac{2}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{2}{r_{12}} + \frac{2}{R}, \quad (1)$$

where

$$i = 1, 2, \quad j = a, b, \\ r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|, \quad R = |\mathbf{R}_a - \mathbf{R}_b|,$$

the subscripts 1,2 designate the two electrons and the subscripts a and b designate the two nuclei. Energy is measured in units of $e^2/2a_0$ rydberg and length in units of $a_0 = 0.529$ Å. The Heitler-London two-particle wave function of the H₂ molecule is written as

$$\psi^\pm(ab, \mathbf{r}_{1a}\mathbf{r}_{2b}) = \frac{1}{[2(1 \pm S^2)]^{1/2}} \\ \times [\phi(\mathbf{r}_{1a})\phi(\mathbf{r}_{2b}) \pm \phi(\mathbf{r}_{1b})\phi(\mathbf{r}_{2a})], \quad (2)$$

where $\phi(\mathbf{r}_{1a})$ is the ground-state wave function of the hydrogen atom. In two dimensions it is written as^{3,6}

$$\phi(\mathbf{r}_{1a}) = \left(\frac{8}{\pi}\right)^{1/2} \alpha \exp(-2\alpha r_{1a}), \quad (3)$$

where $r_{1a} = |\mathbf{r}_1 - \mathbf{R}_a|$, and $\alpha(1/a_0)$ is treated as a variational parameter in a Rosen-type calculation.⁵ In (2) $S = \langle \phi(\mathbf{r}_{1a}) | \phi(\mathbf{r}_{1b}) \rangle$ is the overlap integral.

In two dimensions the lowest-energy state of the H₂

molecule

$$E(\alpha, \mathbf{R}_{ab}) = \langle \psi^+(ab, \mathbf{r}_{1a}\mathbf{r}_{2b}) | H | \psi^+(ab, \mathbf{r}_{1a}\mathbf{r}_{2b}) \rangle \quad (4)$$

can be expressed in terms of the modified Slater integrals¹ $S, K, J, J',$ and K' ,

$$E(\alpha, R) = \frac{2}{(1+S^2)} [2\alpha^2(2-SK-2S^2) \\ + \alpha(-8+2J+4SK+J'+K')] + \frac{2}{R}, \quad (5)$$

where

$$S = 2(\alpha R)^2 [K_0(2\alpha R) + K_1(2\alpha R)/\alpha R], \quad (6)$$

$$K = -8\alpha R K_1(2\alpha R), \quad (7)$$

$$J = -4\alpha [1 - 4\alpha R J_1(2\alpha R) K_0(2\alpha R)], \quad (8)$$

$$J' = \alpha [1/\alpha R - \exp(2.36\alpha R)] \\ \times [1/\alpha R - 3.1\alpha R + 1.1(\alpha R)^2 - 0.3(\alpha R)^3], \quad (9)$$

$$K' = S^2(\alpha R)(0.415\alpha R + 2.776)[1 - \exp(-0.85\alpha R)]/R. \quad (10)$$

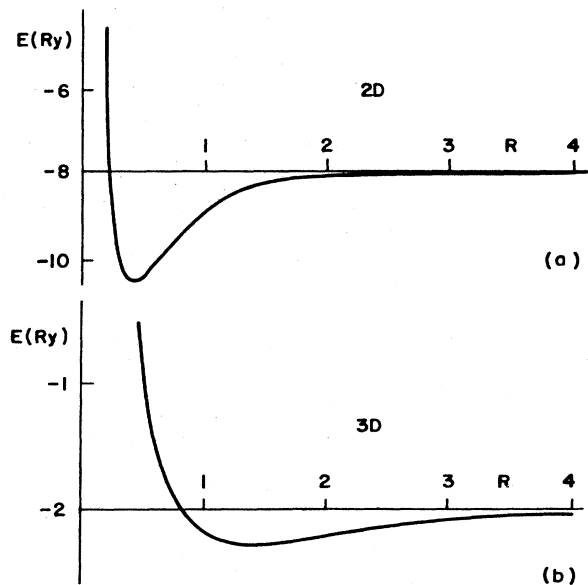


FIG. 1. Energies of the hydrogen molecule, as determined by the variational method, for two dimensions (a), and three dimensions (b).

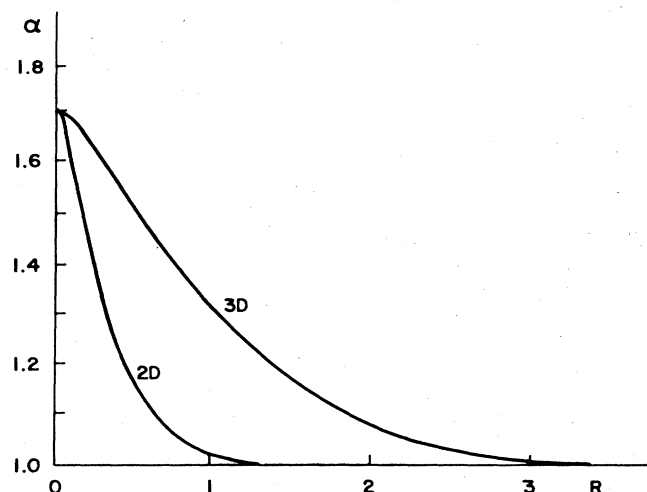


FIG. 2. The variation of the parameter α for 2D and 3D cases of the H_2 molecule.

The integrals K and K' represent, respectively, the electron-hopping energy and exchange effects, and J' represents the electron-correlation effect. K_0 and K_1 are the modified Bessel functions of zero and first order, respectively. J_1 is the Bessel function of first order. Equations (6), (7), and (8) are the analytical expressions of the modified Slater integrals S , K , and J , respectively, while Eqs. (9) and (10) (Ref. 7) correspond to the best-fitted analytical curves of the numerical values of the integrals J' and K' .

All the above 2D energy integrals as well as overlap⁶ are much reduced for $R > 2$ and substantially enhanced for $R < 2$, compared with their values in 3D. The ground-state energy, the equilibrium distance, and the optimum value of α , of the H_2 molecule, are found by a minimization of the energy $\partial E(\alpha, R)/\partial \alpha = 0$, as in the Rosen variational calculation.⁵ In a 2D system, the energy of a neutral hydrogen atom is -4.0 Ry,^{3,6} while for the 3D system it is -1.0 Ry. The 2D H_2 -molecule energy is shown in Fig. 1(a) together with the 3D one [Fig. 1(b)] for the sake of comparison. At the equilibrium distance ($R_0 = 0.37$), $E^{2D} = -10.5$ Ry (for the simple Heitler-London calculation, i.e., $\alpha = 1$, $R_0 = 0.45$, and $E^{2D} = -10$ Ry). For $R \rightarrow \infty$, $E^{2D} = -8.0$ Ry, corresponding to two isolated 2D hydrogen atoms. Thus, we obtain for the dissociation energy the value $D_e = 2.5$ Ry. For comparison, in three dimensions, varying α , $R_0 = 1.41$, $E^{3D} = -2.28$ Ry, and $D_e = 0.28$ Ry (for $\alpha = 1$, $R_0 = 1.64$, and $E^{3D} = -2.24$ Ry). Rosen's⁵ calculation, which also includes a polarization term in (3), gives $D_e = 0.296$ Ry.

The variation of the parameter α , to minimize the energy, is shown in Fig. 2, for 2D and 3D cases. For the latter, the wave function used was $\phi(r_{1a}) = (\alpha^3/\pi)^{1/2} \exp(-\alpha r_{1a})$. For large separation ($R \rightarrow \infty$) both problems reduce to $\alpha = 1$ (isolated hydrogen atoms), and for $R = 0$ (corresponding to a helium atom in this approximation) we have

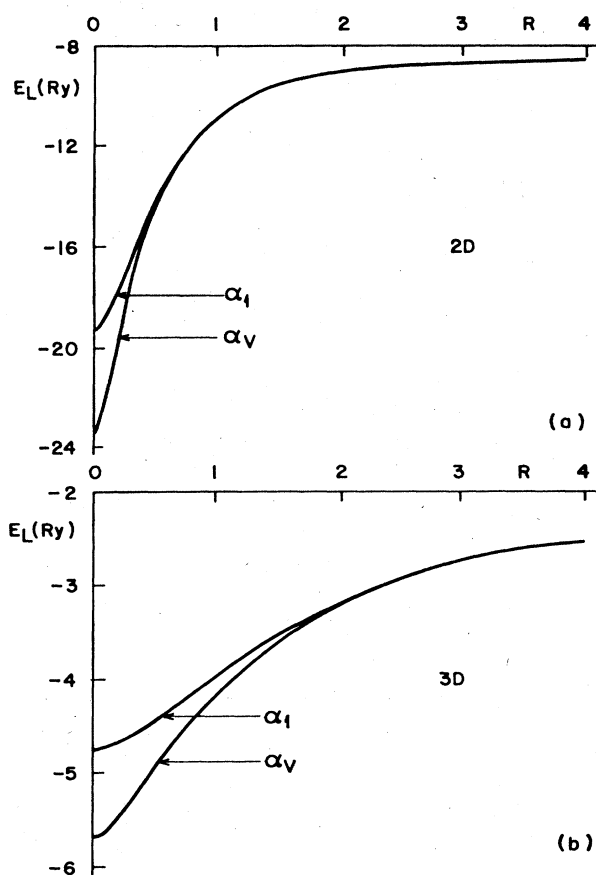


FIG. 3. The electronic energies E_L of the H_2 molecule for two dimensions (a), and three dimensions (b), varying α (α_v) and taking $\alpha = 1$ (α_1).

$\alpha^{2D} = 1.7056$ and $\alpha^{3D} = 1.6875$, respectively.

The excited state of the H_2 molecule corresponds to the minus sign in Eq. (2); it was also calculated. As in three dimensions, no minimum of energy appears in such state. In Figs. 3(a) and 3(b), we show the electronic energies $E_L[E(\alpha, R) - 2/R]$ for the 2D and 3D cases, respectively, for $\alpha = 1$ (α_1) and varying α (α_v). In both cases the difference in energy, at very small interatomic distance R , for α_1 and α_v , is very accentuated, which represents an error of about one-third of the electronic energy. In three dimensions, the variation of the electronic energy with R , in this Rosen-type calculation, follows closely the experimental behavior.¹

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