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Calculation of the hydrogen molecule by means of a parametrization obtained from the hydrogen ion-molecule

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Résumé. — L'énergie électronique de la molécule d'hydrogène est calculée à partir des deux fonctions d'onde les plus simples et les plus typiques (MO-LCAO et VB), en introduisant un facteur de réduction pour la répulsion interélectronique et d'autres paramètres (fonction de la distance internucléaire) modifiant les valeurs moyennes de l'énergie cinétique et de l'énergie potentielle. De tels facteurs sont associés à l'interaction de configuration et certains d'entre eux sont calculés à partir de l'ion moléculaire hydrogène. La comparaison avec les résultats exacts montre un accord satisfaisant concernant le minimum d'énergie, la longueur de liaison et l'énergie de dissociation pour l'état fondamental. Les auteurs discutent quelques extensions possibles de la méthode.

Abstract. — The electronic energy function of the hydrogen molecule is calculated on the basis of the two simplest and most typical wave functions (MO-LCAO and VB) by introducing a reduction factor for the interelectronic repulsion and other functional parameters modifying the expectation values of both kinetic and potential energies. Such factors are associated to the CI contribution and some of them are calculated from the hydrogen ion-molecule. The comparison with the exact results shows a satisfactory agreement in binding energy, bond length and energy minimum values for the ground state. Some possible extensions of the method are discussed.

1. Introduction.

From the very beginning of the development of quantum chemistry, there has been a keen interest in searching simple approximations to describe the ground state $^1\Sigma_g^+$ of H_2 . However, the use of the simplest and well known wave functions (MO-LCAO and VB) gives very poor results for the electronic energy function, and especially the energy minimum location. Then, it is not possible to attain the degree of quality obtained from the self-consistent-field wave function [1], and the exact results [2], if one wishes to keep up the simplicity of the calculation scheme.

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Recently, Fisicaro and Oleari [3] have shown the usefulness of introducing a semiempirical factor to reduce the interelectronic repulsion in the H_2 molecule, in such a way to match the exact total electronic energy and employing the simple MO-LCAO and VB wave functions, in order to calculate significant expectation values. The authors determined the semiempirical factor from the relationship $(-E)^{1/2}$ versus Z for He-like systems, E being the electronic energy and Z the atomic number.

Although Fisicaro and Oleari's procedure introduces in a certain manner a correlation factor in H_2 for the movement of the electrons by a direct transfer of results for He-like systems, the final choice is wholly arbitrary and merely subdued to obtain the optimum matching of the minimum of both functions. Clearly, this procedure does not give a rigorous way of calculating the factor from first principles.

The purpose of this paper is to study the same problem, but from a different point of view with regard to the choice of the semiempirical factor. We employ, as a reference, the ion-molecule H_2^+ to investigate which are the improvements introduced in the simple calculation of H_2 by assuming that the configuration interaction (CI) contributions for the ground state of the former can be transferred to the latter. In what follows, we will call CI contributions the excited state terms in the representation of hydrogen-like eigenfunctions basis set for the ground state, in both approximations (MO-LCAO and VB). Precisely, these terms of the expansion will be transferred from H_2^+ to H_2 . We will see that this different approximation enables us to avoid in a satisfactory manner some previous arbitrarinesses, and furthermore, it yields very good results which are, by far, better than those computed by Fisicaro and Oleari [3]. Finally, our approximation scheme permits one to propose a direct generalization and suitable extensions for more complex systems. We will see later that this extension may be suitable to be applied to bielectronic polyatomic systems and polyelectronic diatomic molecules, within the context of a simple enough treatment.

The paper is organized as follows : section 2 deals with the approximate calculation of the contributions to CI for the ion-molecule H_2^+ as functions depending on R (internuclear distance). In section 3 we display the results of applying the functions deduced in the previous section for H_2^+ , for the ground state calculation of H_2 . In section 4 we show that the introduction of a corrective factor for the interelectronic repulsion term improves significantly the results. Finally, in section 5, we discuss the results in a comparative fashion, and several possible extensions and generalizations are pointed out.

2. H_2^+ as a reference system.

Let us consider the non-relativistic purely electronic Hamiltonian associated to H_2^+

$$H_e = -\frac{\Delta}{2} - r_a^{-1} - r_b^{-1} \quad (\text{in a.u.}), \quad (1)$$

where r_a and r_b are the modulus of position vectors of the electron with respect to the nuclei a and b , respectively. Within the Born-Oppenheimer approximation, the electronic wave function for an internuclear distance R satisfies the equation

$$H_e \phi_e = E(R) \phi_e, \quad (2)$$

where $E(R)$ is the purely electronic energy function and $E(R) + R^{-1}$ the total electronic energy. Equation 2 can be solved exactly by means of a transformation of the equations with elliptic confocal coordinates, and exact results reported with a high degree of accuracy were given by Wind [4] and Schaad and Hicks [5].

The simplest MO-LCAO approximate solution of equation 2 for the ground state is given by

$$\phi_0 = (1s_a(1) + 1s_b(1))/(2(1 + S_{ab}))^{1/2}, \quad (3)$$

where

$$1s_q(1) = k^{3/2} \pi^{-1/2} e^{-kqa}, \quad q = a, b, \quad (4)$$

$$S_{ab} = \langle 1s_a(1) | 1s_b(1) \rangle.$$

and $k = k(R)$ is a variational scaling parameter.

The calculation of $E(R)$ from the function 3 can be accomplished easily [6, 7]. The function 3 represents a first approximation to the problem, and any other improvement ought to consider the CI contribution. Such a contribution may be reached by introduction of other MO-LCAO with hydrogen-like atomic orbitals different from $1s$. In general, this expansion expresses the exact wave function ϕ in a complete basis set $\{\phi_i\}$. Then

$$\phi = \phi_0 + \sum_{i=1}^{\infty} \phi_i, \quad (5)$$

where each ϕ_i ($i = 0, 1, 2, \dots$) contains the corresponding expansion coefficient.

Substituting (5) into (2), we obtain :

$$E(R) = \langle 0 | T | 0 \rangle + 2 \sum_{j=1}^{\infty} \langle 0 | T | j \rangle + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \langle i | T | j \rangle + \langle 0 | V | 0 \rangle +$$

$$+ 2 \sum_{j=1}^{\infty} \langle 0 | V | j \rangle + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \langle i | V | j \rangle, \quad (6)$$

where

$$T = -\frac{1}{2} \Delta, \quad (7)$$

$$V = -(r_a^{-1} + r_b^{-1}). \quad (8)$$

$|0\rangle$ is a MO built up upon the hydrogen-like $1s$ atomic orbital. This molecular orbital may be given in a MO-LCAO approximation, like in equation 3, or it can be contained in the VB approximation.

Now we search to relate the exact results [4] with average values calculated *via* $|0\rangle$, with the purpose of obtaining in such a manner the CI contribution that is present in $E(R)$. If we write equation 6 in the modified form

$$E(R) = \left\{ 1 + 2 \sum_{j=1}^{\infty} \frac{\langle 0 | T | j \rangle}{\langle 0 | T | 0 \rangle} + \sum_{i,j=1}^{\infty} \frac{\langle i | T | j \rangle}{\langle 0 | T | 0 \rangle} \right\} \langle 0 | T | 0 \rangle +$$

$$+ \left\{ 1 + 2 \sum_{j=1}^{\infty} \frac{\langle 0 | V | j \rangle}{\langle 0 | V | 0 \rangle} + \sum_{i,j=1}^{\infty} \frac{\langle i | V | j \rangle}{\langle 0 | V | 0 \rangle} \right\} \langle 0 | V | 0 \rangle, \quad (9)$$

the energy function $E(R)$ can be expressed as

$$E(R) = P(R) \langle 0 | T | 0 \rangle + Q(R) \langle 0 | V | 0 \rangle, \quad (10)$$

with obvious definitions of the functions $P(R)$ and $Q(R)$. Thus, all the higher states contributions are condensed in the functions $P(R)$ and $Q(R)$, which must be determined. Before analysing the calculation of P and Q , we believe proper to comment some of their properties. When any one of these functions is near to the unity, we have

$$P(R)_1 = \frac{E(R) - \langle 0 | V | 0 \rangle}{\langle 0 | T | 0 \rangle}; \quad Q(R) \cong 1 \quad (11a)$$

$$Q(R)_1 = \frac{E(R) - \langle 0 | T | 0 \rangle}{\langle 0 | V | 0 \rangle}; \quad P(R) \cong 1. \quad (11b)$$

Equations 11 are first approximations to the determination of P and Q , because if ϕ_0 is near enough to the exact wave function, then P and Q tend toward one. From a more rigorous viewpoint, if $E(R)$ is the exact energy, the quantum-mechanical virial theorem for diatomic molecules allows us to write the relationship :

$$2 P(R) \langle 0 | T | 0 \rangle = - Q(R) \langle 0 | V | 0 \rangle - R \partial E(R) / \partial R. \quad (12)$$

Then, combining (10) and (12) we deduce the following formulas for the functions $P(R)$ and $Q(R)$ (provided E and $\partial E / \partial R$ are known)

$$P(R) = (-E(R) - R \partial E(R) / \partial R) / \langle 0 | T | 0 \rangle, \quad (13a)$$

$$Q(R) = (2 E(R) + R \partial E(R) / \partial R) / \langle 0 | V | 0 \rangle. \quad (13b)$$

Our aim is to derive a polynomial expression for P and Q in both forms (11) and (13) as R power expansions, by making a fitting to the exact results [4] and the explicit calculation of $\langle 0 | V | 0 \rangle$ and $\langle 0 | T | 0 \rangle$. This fitting is entirely correct because one has discussed in detail the fact that $E(R)$ for diatomic molecules can be written as an expansion in powers of R with respect to the united atoms [8, 9]. As illustrative examples, we present the fitting of two 5th and 6th degree polynomials to match the exact electronic energy (in a.u.), which later on will be used to calculate the functions $P(R)$ and $Q(R)$. We have adjusted the function $E(R)$ for the R range $0.05 \leq R \leq 20.00$ [4], and the results are

$$E(R) = -1.997\,27 + 0.627\,024\,5 R - 0.115\,71 R^2 + 1.048\,308 \times 10^{-1} R^3 - \\ - 4.555\,77 \times 10^{-4} R^4 + 7.578\,593 \times 10^{-6} R^5; \text{ c.c.} = 0.998\,7 \quad (14a)$$

$$E(R) = -2.047\,36 + 0.729\,377\,8 R - 0.166\,381 R^2 + 2.055\,930 \times 10^{-2} R^3 - \\ - 1.396\,56 \times 10^{-3} R^4 + 4.885\,744 \times 10^{-5} R^5 - 6.862\,63 \times 10^{-7} R^6; \text{ c.c.} = 0.999\,7 \quad (14b)$$

where c.c. is the correlation coefficient. It can be seen that both polynomials give poor results for the united-atom electronic energy ($E(0) = -2$ a.u.). However, we will verify that in spite of this deficiency and the fact that the exact curve $E(R)$ versus R is not precisely an appropriate one to be fitted by a polynomial, they offer a relevant information about the minimum total electronic energy, as we will develop in section 3.

From an 8th degree interpolation polynomial determined to calculate $\partial E(R) / \partial R$, we have obtained P_1 , Q_1 , P and Q up to a sixth order polynomial, and results are shown in table I. In addition, we determined the matched polynomials from second to sixth order, and they will be

Table I. — Coefficients of the 6th degree polynomials adjusted for H_2^+ .

Degree	P_1	Q_1	P	Q
0	1.002 361	0.999 374	1.023 282	1.008 700
1	-2.22×10^{-2}	7.69×10^{-3}	-5.79×10^{-3}	-5.02×10^{-3}
2	5.90×10^{-3}	-2.07×10^{-3}	-1.42×10^{-3}	-2.51×10^{-3}
3	-4.81×10^{-4}	1.78×10^{-4}	3.34×10^{-4}	2.97×10^{-4}
4	4.82×10^{-6}	-3.31×10^{-6}	-1.84×10^{-5}	-1.01×10^{-5}
5	9.18×10^{-7}	-2.22×10^{-7}	1.10×10^{-7}	-1.72×10^{-7}
6	-2.79×10^{-8}	7.73×10^{-9}	9.12×10^{-9}	1.09×10^{-8}

applied in the next section to obtain the minimum value of $U(R)$ for H_2 . We can advance that the higher order coefficients diminish quickly, so that it is reasonable to cut off them when one is not particularly interested in large R values of the function $U(R)$.

3. The improved calculation of H_2 .

Now we display the central point of this work, which consists in calculating the electronic energy function of H_2 from the R dependent different functions determined for H_2^+ in the previous section. Let us consider the wave function of H_2 for the non-relativistic Hamiltonian operator (in a.u.)

$$H_h = -\frac{1}{2} A_1 - \frac{1}{2} A_2 - r_{a1}^{-1} - r_{a2}^{-1} - r_{b1}^{-1} - r_{b2}^{-1} + r_{12}^{-1}, \quad (15)$$

built as a product of H_2^+ MO-LCAO wave functions (spin omitted)

$$\phi(1, 2) = \phi(1) \phi(2). \quad (16)$$

It is well known that such a function neglects any correlation between the motion of both electrons. But such electronic correlations can be taken into account by means of the introduction of other configurations ϕ , such as was done in equation 5. Adding the previous expansions for $\phi(i)$ in equation 16, the formula for $\phi(1, 2)$ is a CI-like wave function, in the sense that it includes all the possible products of H_2^+ orbitals for each electron. These orbitals, written as hydrogen-like wave functions within the MO-LCAO or VB approximations, can be considered *in toto* with the P and Q functions. In turn, this means to introduce the best H_2^+ eigenfunctions in a parametric way for determining the average values $\langle T \rangle$ and $\langle V \rangle$ for H_2 . Then, the functional parameters $P(R)$ and $Q(R)$ are introduced in a natural way for H_2 , making

$$E_h = \langle \phi(1) \phi(2) | H_h | \phi(1) \phi(2) \rangle. \quad (17)$$

This manner of introducing the functional factors $P(R)$ and $Q(R)$ via $\phi(1, 2)$ secures that the CI for H_2 is taken into account by means of a similar expansion (Eq. 5) as that introduced previously for H_2^+ . Consequently, we avoid an expansion with variationally adjusted coefficients, such as was done in different approximations [10]. The substitution of equations 1 and 10 into equation 17, gives the formula

$$E_h = 2 P(R) \langle 0 | T_1 | 0 \rangle + 2 Q(R) \langle 0 | V_1 | 0 \rangle + \langle \phi(1) \phi(2) | r_{12}^{-1} | \phi(1) \phi(2) \rangle, \quad (18)$$

where $|0\rangle$ is the state vector associated to the ground state of H_2^+ in some simple approximation, and

$$\left. \begin{aligned} T_1 &= -\frac{1}{2} A_1 \\ V_1 &= -r_{a1}^{-1} - r_{b1}^{-1} \end{aligned} \right\} \quad (19)$$

Remaining within a simple scheme of calculation, we rewrite equation 18 in the approximate form

$$E_h = 2 P(R) \langle 0 | T_1 | 0 \rangle + 2 Q(R) \langle 0 | V_1 | 0 \rangle + \langle 00 | r_{12}^{-1} | 00 \rangle, \quad (20)$$

and we choose as wave functions $|00\rangle$ the simplest ones associated to the MO-LCAO and VB methods, i.e.

$$|00\rangle_{\text{MO}} = N[1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)] \quad (21a)$$

$$|00\rangle_{\text{VB}} = M[1s_a(1) 1s_b(2) + 1s_a(2) 1s_b(1)] \quad (21b)$$

where N and M are the corresponding normalization factors.

An immediate and direct interpretation of equation 20 is possible : the term $\langle 00 | r_{12}^{-1} | 00 \rangle$ is the simplest way of considering the interelectronic repulsion, starting from the H_2^+ wave functions which are parametrized with respect to the exact results.

4. A further improvement on the calculation of H_2 .

Now, we can go a step further regarding the approximation scheme developed in the previous section. The use of polynomials P and Q constitutes a variational-like approximation since we have brought in the H_2^+ MO in order to calculate the H_2 energy. To improve this approach, we can introduce, in addition to the functions P and Q , a corrective factor f for the interelectronic repulsion term.

Obviously, this modification sets aside the variational character of the results for E_h .

The factor f cannot be taken from the H_2^+ results, because it is closely related to correlation effects [3]. We follow here a similar procedure to that presented by Fiscaro and Oleari [3] to compute this semiempirical factor. If E is the electronic energy of helium-like atoms, it is deduced at once that the expectation value of the Hamiltonian operator corresponding to such kind of atoms with a scaled 1s AO is given by

$$(-E)^{1/2} = uZ - v, \quad (22)$$

where

$$u = \langle r_i^{-1} \rangle \langle -\Delta_i \rangle^{-1/2} = 1, \\ v = \frac{1}{2} \langle r_{12}^{-1} \rangle \langle -\Delta_i \rangle^{-1/2} = \frac{5}{16}.$$

Following Fiscaro and Oleari, we plotted $(-E)^{1/2}$ versus Z , and we obtained a linear behaviour, with a very small standard deviation. From the experimental data of ionization potentials [11], the result calculated (including atoms up to $Z = 13$, which yields the largest value for the correlation coefficient) is

$$(-E)^{1/2} = 1.000\,020\,Z - 0.303\,535; \quad \text{c.c.} = 0.999\,995\,4, \quad (23)$$

and enables us to deduce a correction factor f for the « effective » interelectronic repulsion $\langle r_{12}^{-1} \rangle$:

$$f = 0.303\,535/(5/16) = 0.971\,313.$$

This numerical value is quite different from that reported previously [3], since we have employed more accurate ionization potential data. Now we have the necessary elements to study the H_2 molecule within the present calculation scheme. It is important to keep in mind that it consists in the inclusion, in a more proper way, of the correction factor f of helium-like systems for the interelectronic repulsion in H_2 , with the use of the functions $P(R)$ and $Q(R)$.

The procedure is clearly different from that presented by Fiscaro and Oleari [3] because they fitted the f value in order to match the exact energy value, using different simple wave functions. Naturally, such a method does not offer any possibility for determining f from first principles, and a different optimum f -value must be used for every approximate wave function.

The introduction of the correction factor f allows us to write the electronic energy function E_h in a more appropriate manner as

$$E_h = 2P(R)\langle 0 | T_1 | 0 \rangle + 2Q(R)\langle 0 | V_1 | 0 \rangle + f\langle 00 | r_{12}^{-1} | 00 \rangle. \quad (24)$$

The idea of reducing the electron repulsion integrals in molecules is not new. Julg [12] proposed a way to calculate the decreasing of the bielectronic integrals as an R -function. When $R \rightarrow 0$, the reduction factor f for a J_{1s1s} integral (which is our actual concern) is determined as

$$f \sim \frac{1}{N} \sum_{i=2}^N \frac{(J_{1s1s})_i}{Z_i},$$

which gives $f \sim 0.5$. $(J_{1s1s})_i$ is the value of the Coulomb integral for the atom with nuclear charge Z_i of the helium-like series. Evidently, our procedure gives a not so drastic reduction, and it is calculated in a quite different way.

The procedure adopted to reduce the integral $\langle 00 | r_{12}^{-1} | 00 \rangle$ is wholly suitable for our actual purpose : to reduce the expectation value of the electronic repulsion when E_h is approximated by means of two functions (P and Q) that introduce parametrically the H_2^+ eigenstates, and consequently cannot take into account in a proper manner the correlation effects in H_2 .

We will compare the results of applying equation 24 with and without the factor f (Eq. 20). In order to provide a correct comparison among the different approximations presented in this work, we display in table II the numerical values of $(-E_h)_{\min}$, $R_{\min}$ and D_e (spectroscopic dissociation energy) for self-consistent and exact calculations, as well as for the naive wave functions MO-LCAO and VB ($P = Q = f = 1$). Table III shows the results for H_2 from the MO-LCAO wave function (21a) and using P_1 (with $Q_1 = 1$), Q_1 (with $P_1 = 1$), and P, Q matched with the virial theorem results of H_2^+ .

Table II. — *Parameters of the H_2 molecule for the internuclear distance corresponding to the minimum energy : comparative results for different approximations.*

Function	$R_{\min}$ (a.u.)	$(-E_h)_{\min}$ (a.u.)	D_e (eV)
MO-LCAO	1.391	1.129 493	3.524
VB	1.439 4	1.134 960	3.672
SCF [1]	1.389	1.133 665	3.637
Exact [2]	1.401 1	1.174 475	4.748

Table III. — *Results for the MO-LCAO ground state function of H_2 .*

Degree	P_1			Q_1			P, Q		
	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e
2	1.360	1.150 4	4.092	1.362	1.153 8	4.185	1.361	1.155 6	4.234
3	1.368	1.148 6	4.042	1.372	1.151 6	4.126	1.365	1.154 8	4.213
4	1.382	1.148 3	4.036	1.388	1.151 4	4.119	1.381	1.154 6	4.028
5	1.386	1.149 7	4.072	1.394	1.153 0	4.164	1.386	1.156 6	4.262
6	1.390	1.150 0	4.083	1.398	1.153 2	4.168	1.392	1.156 6	4.261

In table IV we give identical information as in table III, but now the computations were made with the VB wave function 21b, and for the different degrees of the approximation polynomials. Table V offers the results for the function 24 with $f = 0.971\ 313$ and P, Q fitted to the virial

theorem using the wave functions 21a and 21b. Finally, in table VI we report the characteristic values averaged over the fitting polynomials which were presented through table III-V. The comparison is complemented with the plots given in figures 1-4 of $E(R)$ functions for the complete range of R values, and for different approximation schemes.

Table IV. — *Results for the VB ground state function of H_2 .*

Degree	P_1			Q_1			P, Q		
	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e
2	1.398	1.158 8	4.321	1.403	1.159 7	4.347	1.403	1.160 6	4.369
3	1.408	1.156 8	4.267	1.414	1.157 6	4.289	1.410	1.159 2	4.332
4	1.428	1.156 9	4.269	1.435	1.157 7	4.291	1.429	1.159 3	4.335
5	1.434	1.158 5	4.313	1.439	1.159 5	4.340	1.435	1.161 2	4.382
6	1.439	1.159 1	4.329	1.444	1.159 7	4.346	1.442	1.161 3	4.389

Table V. — *Results for the MO-LCAO and VB functions employing equation 24.*

Degree	MO-LCAO			VB		
	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e
2	1.350	1.174 5	4.749	1.381	1.177 9	4.841
3	1.354	1.173 7	4.727	1.389	1.176 5	4.803
4	1.369	1.173 4	4.719	1.408	1.176 5	4.803
5	1.375	1.175 4	4.772	1.414	1.178 4	4.854
6	1.379	1.175 3	4.770	1.419	1.178 4	4.854

Table VI. — *Averaged values, over the adjusted polynomials, of the parameters for the internuclear distance corresponding to the minimum energy of the H_2 molecule.*

Function	P_1			Q_1			P, Q			P, Q, f		
	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e	$R_{\min}$	$-E_{\min}$	D_e
MO-LCAO	1.377	1.149 4	4.065	1.383	1.152 6	4.152	1.377	1.155 6	4.236	1.365	1.174 5	4.747
VB	1.421	1.158 0	4.300	1.427	1.158 8	4.323	1.424	1.160 3	4.362	1.402	1.177 5	4.831

5. Discussion.

The comparison of results in tables III-V shows clearly that they are not very dependent on the R degree for the fitting polynomials with respect to $E_{\min}$, but a more significant dependence is noted with respect to $R_{\min}$. Taking into account this fact, the direct comparison of tables II and VI shows plainly the high accuracy for $E_{\min}$ when it is calculated with the polynomials instead of the

Fig. 1. — Comparison of the different approximations using the MO-LCAO function and the 6th degree polynomials. *a*) Simple MO-LCAO function (Eq. 21*a*). *b*) Equation 11*a* with the 6th degree polynomial $P(R)_1$. *c*) Equation 11*b* with the 6th degree polynomial $Q(R)_1$. *d*) Equations 13*a* and 13*b* with the 6th degree polynomials P and Q . *e*) Exact result [2].

mere use of (21*a*) and (21*b*) ($P = Q = f = 1$) and even of the self-consistent approximation. One should also remark the improvement for $R_{\min}$ with the function 21*b*, although it is not so for the function 21*a*. The amelioration is noticeable, too, for D_e values.

Furthermore, it is seen that by way of the sole use of the polynomials P and Q fitted with the virial theorem, the results for $-E_{\min}$ are in the 1.15-1.16 hartrees range and a difference of 0.01 hartree with respect to the exact results must be attached to CI corrections for the interelectronic repulsion and to correlation effects. This is confirmed by the fact that the insertion of f in

Fig. 2. — Comparison of the different approximations using the VB function and the 6th degree polynomials. *a*) Simple VB function (Eq. 21*b*). *b*) Equation 11*a* with the 6th degree polynomial $P(R)_1$. *c*) Equation 11*b* with the 6th degree polynomial $Q(R)_1$. *d*) Equations 13*a* and 13*b* with the 6th degree polynomials P and Q . *e*) Exact result [2].

the function 24 removes the differences in $R_{\min}$ and $-E_{\min}$ in a very acceptable manner, employing functions 21*a*-21*b* respectively. The importance of this last result must be stressed because the characteristic parameters associated to the minimum of the function $E(R)$ are manifestly sensitive to the f values, and the better results correspond to the strict utilization of the value calculated from the fitting of the helium-like systems. However, it seems improper to include such a f value in order to study any other property outside of the minimum region, because the electronic correlation (i.e. the factor f) depends on R (see Fig. 4).

Fig. 3. — Comparison of exact and SCF results with the MO-LCAO and VB approximations using the polynomials P and Q adjusted with the virial theorem. *a*) SCF function with nine terms [1]. *b*) MO-LCAO function 21*a* with the 6th degree polynomials in equations 13*a* and 13*b*. *c*) VB function 21*b* with the 6th degree polynomials P and Q in equations 13*a* and 13*b*. *d*) Exact result [2].

In summary, we have discussed the convenience of introducing parametrized functions by means of the polynomials P and Q for many-electron systems, where these polynomials are determined from the exact results of the H_2^+ system (which is exactly solvable within the Born-Oppenheimer approximation). The results obtained for the most relevant parameters of H_2 are highly satisfactory. The method presented in this communication can be considered a generalization of that due to Fiscaro and Oleari [3]. Besides, the quality of the results obtained for H_2 suggest that it would be worth to extend this scheme of calculation for other more complex

Fig. 4. — Comparison of exact and SCF results with the MO-LCAO and VB approximations using the polynomials P and Q adjusted with the virial theorem and the correction factor f . a) SCF function with nine terms. b) MO-LCAO function 21a with equation 24 for the 6th degree polynomials P and Q (Eqs. 13a and 13b). c) VB function 21b with equation 24 for the 6th degree polynomials P and Q (Eqs. 13a and 13b). d) Exact result [2].

systems. In principle, the procedure may be generalized for bielectronic polyatomic molecules, by use of some reduction factor f and obtaining the parameters P and Q from the exact solution of the analogous monolectronic system with identical geometry. The present method may offer an alternative procedure, in the case of polyelectronic diatomic molecules, to compute the energy at the equilibrium position by means of a simplifying parametrization of the bielectronic integrals. A possible manner to achieve this proposal is to apply local electron-electron energy density functionals [13-15].

At present this kind of analysis is being made in our laboratory and results will be published elsewhere in a forthcoming paper.

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