

## Are the program packages for molecular structure calculations really black boxes?

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**Abstract:** In this communication it is shown that the widely held opinion that compact program packages for quantum–mechanical calculations of molecular structure can safely be used as black boxes is completely wrong. In order to illustrate this, the results of computations of equilibrium bond lengths, vibrational frequencies and dissociation energies for all homonuclear diatomic molecules involving the atoms from the first two rows of the Periodic Table, performed using the Gaussian program package are presented. It is demonstrated that the sensible use of the program requires a solid knowledge of quantum chemistry.

**Keywords:** molecular structure calculations, Gaussian, dissociation energy.

### INTRODUCTION

Some thirty years ago, when the senior author of this paper began working in the field of quantum chemistry and his coworkers were not yet born, no compact program packages for performing molecular structure calculations were available. More precisely, several scientists had developed their own algorithms for solving approximately the electronic Schrödinger equation but even for the members of their working groups the use of these programs was impossible without deep knowledge of quantum chemistry, group theory, linear algebra and related topics. As a rule, any step beyond the computation of equilibrium geometries, vertical electronic spectra and potential energy surfaces (*e.g.*, consideration of nuclear dynamics, spin-orbit or non-adiabatic couplings) was connected with the necessity of inventing new methods and writing by oneself the corresponding computer programs. In the meantime considerable progress has been achieved and now several complete program packages for molecular structure calculations, such as Gaussian, MOLPRO, MOLCAS and TURBOMOL, developed by a number of experts in quantum chemistry, can be provided and, thanks to the corresponding more or less detailed manuals, employed by a broad class of users. A

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consequence of this development is that nowadays many chemists, without profound knowledge of quantum mechanics, can (or at least believe they are able to) carry out quantum–chemical computations to support or explain their experimental results. The goal of the present study is to show that the “blind” use of these program packages and uncritical belief in the reliability of the results produced by them can be very dangerous.

COMPUTATION OF STRUCTURE PARAMETERS FOR DIATOMIC HOMONUCLEAR MOLECULES INVOLVING THE ATOMS FROM THE FIRST AND SECOND ROW OF THE PERIODIC TABLE, BY MEANS OF THE GAUSSIAN PROGRAM PACKAGE

The primary goal of the present study was not to achieve the best possible numerical results obtainable with the Gaussian program package<sup>1</sup> but instead to discuss the results of typical results and their accuracy. Presented here are the equilibrium bond lengths, harmonic vibrational frequencies and the dissociation energies for all homonuclear diatomic (neutral) molecules involving the atoms from the first two rows of the Periodic Table, obtained by means of the restricted Hartree–Fock (RHF) formalism, density functional theory (DFT) and, in the case of the H<sub>2</sub> molecule, using the configuration interaction (CI) approach. The atomic orbital (AO) basis 6–311+G(d,p) and the B3LYP functional were employed. The results are presented in Table I. They are compared with the corresponding experimental findings taken from Ref. 2.

TABLE I. Equilibrium bond lengths ( $r_e$ ), harmonic vibrational frequencies ( $\omega$ ) and dissociation energies ( $D_0^0$ ) for homonuclear diatomic molecules involving the atoms from the first two rows of the Periodic Table, obtained by means of the Gaussian program package (RHF, DFT) and derived from experimental data (exp.).<sup>2</sup> The symbol “–” means that the experimental or theoretical result is missing – the latter because the energy of the isolated atoms was not computed to be higher than that of the molecule and/or the potential curve did not converge to a constant value at the dissociation limit (actually at the internuclear distance of 20 Å).

| Molecule        | GS            | El. conf.                                 | Method | $r_e / \text{Å}$   | $\omega / \text{cm}^{-1}$ | $D_0^0 / \text{eV}$  | $D_0^0 / \text{eV}$<br>$2E_{\text{at}} - E_{\text{mol}}$ |
|-----------------|---------------|---|--------|--------------------|---------------------------|----------------------|--|
| H <sub>2</sub>  | $1\Sigma_g^+$ | $(1\sigma_g)^2$                           | RHF    | 0.735              | 4595                      | 10.80                | 3.340  |
|                 |               |   | DFT    | 0.744              | 4421                      | 7.400                | 4.500  |
|                 |               |   | exp.   | 0.741              | 4401                      | 4.478                | 4.478  |
| He <sub>2</sub> | $1\Sigma_g^+$ | $(1\sigma_g)^2(1\sigma_u)^2$              | RHF    | 3.368              | 13                        | –                    | –  |
|                 |               |   | DFT    | 4.668              | 9.0                       | –                    | –  |
|                 |               |   | exp.   | 2.970 <sup>a</sup> | –                         | 0.00090 <sup>a</sup> | 0.0090 <sup>a</sup>                                      |
| Li <sub>2</sub> | $1\Sigma_g^+$ | $[\text{He}_2](2\sigma_g)^2$              | RHF    | 2.785              | 337                       | –                    | 0.15   |
|                 |               |   | DFT    | 2.705              | 343                       | 1.67                 | 0.88   |
|                 |               |   | exp.   | 2.673              | 351                       | 1.04                 | 1.04   |
| Be <sub>2</sub> | $1\Sigma_g^+$ | $[\text{He}_2](2\sigma_g)^2(2\sigma_u)^2$ | RHF    | 1.810              | 921                       | –                    | –  |
|                 |               |   | DFT    | 2.491              | 285                       | 0.17                 | 0.17   |
|                 |               |   | exp.   | –                  | –                         | –                    | –  |
| B <sub>2</sub>  | $3\Sigma_g^-$ | $[\text{Be}_2](1\pi_u)^2$                 | RHF    | 1.639              | 942                       | –                    | 0.80   |
|                 |               |   | DFT    | 1.616              | 1002                      | 2.52                 | 2.52   |
|                 |               |   | exp.   | 1.590              | 1051                      | 3.00                 | 3.00   |

TABLE I. Continued

| Molecule        | $GS$          | El. conf.  | Method | $r_e / \text{\AA}$ | $\omega / \text{cm}^{-1}$ | $D_0^0 / \text{eV}$  | $D_0^0 / \text{eV}$<br>$2E_{\text{at}} - E_{\text{mol}}$ |
|-----------------|---------------|--|--------|--------------------|---------------------------|----------------------|--|
| C <sub>2</sub>  | $1\Sigma_g^+$ | $[Be_2](1\pi_u)^4$   | RHF    | 1.245              | 1907                      | –                    | 0.29   |
|                 |               |  | DFT    | 1.252              | 1868                      | 10.0                 | 4.98   |
|                 |               |  | exp.   | 1.242              | 1854                      | 6.21                 | 6.21   |
| C <sub>2</sub>  | $1\Sigma_g^+$ | $[Be_2](1\pi_u)^4$   | RHF    | 1.245              | 1907                      | –                    | 0.29   |
|                 |               |  | DFT    | 1.252              | 1868                      | 10.0                 | 4.98   |
|                 |               |  | exp.   | 1.242              | 1854                      | 6.21                 | 6.21   |
| N <sub>2</sub>  | $1\Sigma_g^+$ | $[Be_2](1\pi_u)^4(3\sigma_g)^2$                              | RHF    | 1.071              | 2735                      | 32.10                | 4.830  |
|                 |               |  | DFT    | 1.096              | 2445                      | 18.02                | 9.600  |
|                 |               |  | exp.   | 1.098              | 2359                      | 9.759                | 9.759  |
| O <sub>2</sub>  | $3\Sigma_g^-$ | $[Be_2](1\pi_u)^4(3\sigma_g)^2$<br>$(1\pi_g)^2$              | RHF    | 1.152              | 2025                      | 20.43                | 0.980  |
|                 |               |  | DFT    | 1.206              | 1634                      | 10.19                | 5.09   |
|                 |               |  | exp.   | 1.208              | 1580                      | 5.115                | 5.12   |
| F <sub>2</sub>  | $1\Sigma_g^+$ | $[Be_2](1\pi_u)^4(3\sigma_g)^2$<br>$(1\pi_g)^4$              | RHF    | 1.329              | 1225                      | –                    | –  |
|                 |               |  | DFT    | 1.409              | 982.0                     | 5.230                | 1.32   |
|                 |               |  | exp.   | 1.412              | 916.6                     | 1.602                | 1.60   |
| Ne <sub>2</sub> | $1\Sigma_g^+$ | $[Be_2](1\pi_u)^4(3\sigma_g)^2$<br>$(1\pi_g)^4(3\sigma_u)^2$ | RHF    | 3.3                | 28                        | –                    | –  |
|                 |               |  | DFT    | 3.1                | 39                        | –                    | –  |
|                 |               |  | exp.   | 3.1                | 14 <sup>b</sup>           | 0.00202 <sup>b</sup> | 0.00202 <sup>b</sup>                                     |

<sup>a</sup>Derived from electron scattering experiments; <sup>b</sup>uncertain results

Before going into the qualitative analysis of the results shown in Table I, some trends should be noted. The equilibrium bond lengths are generally quite reasonably computed by both the HF and DFT approach, with the DFT results being superior in most cases. In the case of the noble-gas molecules He<sub>2</sub> and Ne<sub>2</sub>, as well as for Be<sub>2</sub>, the reliability of both the theoretical and experimental results is questionable. The same trends are found for the harmonic vibrational frequencies, except in the case of H<sub>2</sub>, B<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub>, for which the HF results are inaccurate. The dissociation energies were computed in two different ways: a) as the energy difference between the dissociation limit of the molecular potential energy curve and the zeroth vibrational level and b) as the difference between the energy of the isolated atoms in their ground states and that of the molecule in its equilibrium geometry, corrected by the zero-point vibrational energy. The first set of results is generally in very bad agreement with the experimental data in both the HF and DFT calculations. The HF results obtained by applying the second approach are again poor (they are close to those generated in the HF calculations employing saturated AO basis sets<sup>3</sup>), while their DFT counterparts are (except for C<sub>2</sub> and F<sub>2</sub>) in reasonable agreement with the experimental values.

#### INTERPRETATION OF THE RESULTS OF COMPUTATIONS

##### *Correlation energy error*

As seen by inspection of Table I, the most serious computation errors for the molecules considered in the present study concern their dissociation energies. In this and the following subsection, explanations of the reasons for this are given.<sup>4,5</sup>

The HF energy of the ground electronic state of  $N_2$  at its equilibrium geometry is computed to be  $-2965.19$  eV. This value is very close to the HF limit (*i.e.*, to the HF energy obtained using an infinitely large basis set) of  $-2965.62$  eV and simultaneously 99.5 % of the exact non-relativistic energy,  $-2980.58$  eV. For the SCF energy of a nitrogen atom, a value of  $-1480.10$  is obtained; the HF limit is  $-1480.22$ , and the exact energy  $-1485.39$  eV. Thus, the energy of the atom is calculated with a relative error of only 0.35 %. In spite of this, the HF dissociation energy obtained as  $E(2N) - E(N_2)$ , 5.00 eV (or 4.83 eV if the energy of the zeroth vibrational level is taken into account) is only about 50 % of the experimental value ( $E_{\text{dis}} = 9.90$  eV). The problem is namely that the experiments give information not about the total energies but about the energy differences and the latter are unfortunately only a very small part (say 1 %) of the total energy. Thus, an error of 1 % in the total energy can cause a huge error (say 50 %) in the energy difference actually measured. Moreover, if the dissociation energy is defined as the energy difference between the dissociation limit of the potential energy curve and its minimum, the HF value becomes as large as 32.10 eV!

The reasons for such an inaccuracy of the computed dissociation energies lie in the nature of the HF approach. First, this method assumes the total electronic wave function as an (anti-symmetric) product of individual one-electron wave functions (spin-orbitals) and as such it is not capable of taking properly into account the correlation of electronic motions; the real mutual interaction of individual electrons is simulated by an interaction of one particular electron with the mean field produced by all the other ones. This approximation works well as long as the electrons are far away from one another. However, when two electrons build a molecular orbital (MO), *i.e.*, when they form a chemical bond, they are found close to each other and the HF philosophy, which allows them to be arbitrarily close to each other, becomes unrealistic. The quantitative measure of this effect is the “dynamical correlation error”, being of different magnitude for different atoms and molecules, but also for different electronic states of the same molecular or atomic system. The electronic configuration of the nitrogen molecule at its equilibrium geometry represents a “closed shell” system (see Table I); the ground state of the nitrogen atom is, on the other hand,  $1s^2 2s^2 2p^3$  ( $^4S_{3/2}$ ), *i.e.*, two nitrogen atoms involve six open shells. This means that the dissociation of  $N_2$  into two N atoms is characterized by the breaking of three bonds and this causes extremely different correlation errors when calculating these systems in the framework of the HF approach.

Another, usually even more serious, drawback of the HF method is a consequence of representing the electronic wave function by a Slater determinant corresponding to a particular electronic configuration. The closed-shell Slater determinant, reasonably approximating the electronic wave function not far from the equilibrium geometry, is totally inadequate for describing two open-shell

nitrogen atoms in their ground states. The closed-shell determinant employed leads thus into a “wrong” (much higher energy) dissociation channel.

The DFT energy at the equilibrium geometry of  $N_2$  is computed to be  $-2981.12$ , *i.e.*,  $-2980.97$  eV, with the zero-point vibrational energy correction. Thus the calculation error is only 0.01 %. For the energy of an isolated nitrogen atom the applied DFT approach gives  $-1485.68$  eV (error of 0.02 %). A consequence of this improved accuracy, when compared with the HF treatment, is the dissociation energy  $E(2N) - E(N_2) = 9.75$  (9.60) eV, which is in close agreement with the experimental value. The high accuracy of the DFT results in this case is a consequence of the fact that this method properly accounts for the correlation of the electronic motions. Note that the DFT results for absolute energies are in the present case slightly below the exact results; this may occur because the DFT (as opposed to the HF method) is not a completely variational approach. However, if the dissociation energy is computed as the difference between the asymptotic energy of the potential curve for  $N_2$  and its minimum, the wrong value of 18.17 (18.02) eV is obtained. This means that the DFT method does not eliminate the “non-dynamical correlation error”.

#### *Dissociation of the hydrogen molecule*

In this subsection, the problem of non-dynamic correlation is discussed on the example of the hydrogen molecule. The non-relativistic electronic Hamiltonian (involving also the nuclear repulsion term) for the hydrogen molecules can be written in the form (atomic units,  $m_e \equiv 1$ ,  $e \equiv 1$ ,  $\hbar \equiv 1$ , are used throughout this paper):

$$H = h_1 + h_2 + h_{12} + \frac{1}{r_{AB}} \quad (1)$$

where

$$\begin{aligned} h_1 &= -\frac{1}{2} \Delta_1 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}}, \\ h_2 &= -\frac{1}{2} \Delta_2 - \frac{1}{r_{A2}} - \frac{1}{r_{B2}}, \\ h_{12} &= \frac{1}{r_{12}}. \end{aligned} \quad (2)$$

The nuclei are denoted by  $A$  and  $B$  and the electrons by 1 and 2.  $h_1$  and  $h_2$  are one-electron operators, while  $h_{12}$  is a two-electron operator. The Hamiltonian partitioned in such a form is adjusted to molecular orbital approaches, such as HF (and also DFT in its practical applications). For the discussion to follow, one can restrict oneself to the use of the minimal basis of AOs for the representation of the MOs; thus it is assumed that:

$$\begin{aligned}\Psi_1 &= \frac{1}{\sqrt{2(1+S)}}(s_A + s_B) \equiv \sigma_g, \\ \Psi_2 &= \frac{1}{\sqrt{2(1-S)}}(s_A - s_B) \equiv \sigma_u,\end{aligned}\quad (3)$$

where  $\Psi_1$  and  $\Psi_2$  are the MOs,  $s_A$  and  $s_B$  the  $1s$  AOs centered on the nuclei  $A$  and  $B$ , respectively, and

$$S \equiv \langle s_A | s_A \rangle \equiv \int s_A^* s_B d\vec{r} \quad (4)$$

is the overlap integral. According to the Pauli principle, the two electrons of the hydrogen molecule can be distributed in six ways among the MOs  $\sigma_g$  and  $\sigma_u$ , resulting in six approximate total electronic functions in form of the Slater determinants:

$$\begin{aligned}\Phi_1 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g \alpha(1) & \sigma_g \beta(1) \\ \sigma_g \alpha(2) & \sigma_g \beta(2) \end{vmatrix} = \sigma_g(1)\sigma_g(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \equiv 1^1 \Sigma_g^+, \\ \Phi_2 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g \alpha(1) & \sigma_u \alpha(1) \\ \sigma_g \alpha(2) & \sigma_u \alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)] \alpha(1)\alpha(2) \equiv {}^3 \Sigma_u^+ (M_S = 1), \\ \Phi'_3 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g \alpha(1) & \sigma_u \beta(1) \\ \sigma_g \alpha(2) & \sigma_u \beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\sigma_g(1)\alpha(1)\sigma_u(2)\beta(2) - \sigma_u(1)\beta(1)\sigma_g(2)\alpha(2)], \\ \Phi'_4 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g \beta(1) & \sigma_u \alpha(1) \\ \sigma_g \beta(2) & \sigma_u \alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\sigma_g(1)\beta(1)\sigma_u(2)\alpha(2) - \sigma_u(1)\alpha(1)\sigma_g(2)\beta(2)], \\ \Phi_5 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_g \beta(1) & \sigma_u \beta(1) \\ \sigma_g \beta(2) & \sigma_u \beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)] \beta(1)\beta(2) \equiv {}^3 \Sigma_u^+ (M_S = -1), \\ \Phi_6 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \sigma_u \alpha(1) & \sigma_u \beta(1) \\ \sigma_u \alpha(2) & \sigma_u \beta(2) \end{vmatrix} = \sigma_u(1)\sigma_u(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \equiv 2^1 \Sigma_g^+.\end{aligned}\quad (5)$$

$\alpha$  and  $\beta$  represent the spin Eigen functions of individual electrons. As indicated in Eq. (5), the Slater determinants  $\Phi_1$ ,  $\Phi_2$ ,  $\Phi_5$  and  $\Phi_6$  are automatically Eigen functions of the total orbital and spin angular momenta;  $\Phi'_3$  and  $\Phi'_4$  are not, but these are their linear combinations,

$$\begin{aligned}\Phi_3 &\equiv \frac{1}{\sqrt{2}}(\Phi'_3 + \Phi'_4) = \frac{1}{\sqrt{2}} [\sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \equiv {}^3 \Sigma_u^+ (M_S = 0), \\ \Phi_4 &\equiv \frac{1}{\sqrt{2}}(\Phi'_3 - \Phi'_4) = \frac{1}{\sqrt{2}} [\sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \equiv 1^1 \Sigma_u^+.\end{aligned}\quad (6)$$

In the vicinity of its equilibrium geometry, the ground electronic state of the hydrogen molecule is approximately described by the wave function  $\Phi_1$ , corresponding to the doubly populated lower-energy MO,  $\sigma_g$ . Since the Hamiltonian does not involve the spin coordinates, the energy of this state is given by:

$$\langle E_1 \rangle = \langle \Phi_1 | H | \Phi_1 \rangle = \langle \sigma_g(1)\sigma_g(2) | h_1 + h_2 + h_{12} + \frac{1}{r_{AB}} | \sigma_g(1)\sigma_g(2) \rangle = 2h_g + J_{gg} + \frac{1}{r_{AB}}, \quad (7)$$

where

$$\begin{aligned} h_g &\equiv \langle \sigma_g(1) | h_1 | \sigma_g(1) \rangle = \langle \sigma_g(2) | h_2 | \sigma_g(2) \rangle, \\ J_{gg} &\equiv \langle \sigma_g(1)\sigma_g(2) | h_{12} | \sigma_g(1)\sigma_g(2) \rangle. \end{aligned} \quad (8)$$

The lowest-lying excited state is  $1^3\Sigma_u^+$ , corresponding to the wave functions  $\Phi_1$ ,  $\Phi_2$  and  $\Phi_5$ . Its energy is:

$$\begin{aligned} \langle E_{2,3,5} \rangle &= \langle \Phi_2 | H | \Phi_2 \rangle = \langle \Phi_3 | H | \Phi_3 \rangle = \langle \Phi_5 | H | \Phi_5 \rangle \\ &= \frac{1}{2} \langle \sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2) | h_1 + h_2 + h_{12} + \frac{1}{r_{AB}} | \sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2) \rangle \\ &= h_g + h_u + J_{gu} - K_{gu} + \frac{1}{r_{AB}}, \end{aligned} \quad (9)$$

with

$$\begin{aligned} h_u &\equiv \langle \sigma_u(1) | h_1 | \sigma_u(1) \rangle = \langle \sigma_u(2) | h_2 | \sigma_u(2) \rangle, \\ J_{gu} &\equiv \langle \sigma_g(1)\sigma_u(2) | h_{12} | \sigma_g(1)\sigma_u(2) \rangle = J_{ug}, \\ K_{gu} &\equiv \langle \sigma_g(1)\sigma_u(2) | h_{12} | \sigma_u(1)\sigma_g(2) \rangle = K_{ug}. \end{aligned} \quad (10)$$

The second excited state is  $1^1\Sigma_u^+$  with the energy:

$$\begin{aligned} \langle E_4 \rangle &= \langle \Phi_4 | H | \Phi_4 \rangle = \frac{1}{2} \langle \sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2) | h_1 + h_2 + h_{12} + \frac{1}{r_{AB}} | \sigma_g(1)\sigma_u(2) + \sigma_u(1)\sigma_g(2) \rangle \\ &= h_g + h_u + J_{gu} + K_{gu} + \frac{1}{r_{AB}}, \end{aligned} \quad (11)$$

and, finally, the third excited state corresponds to  $\Phi_6$  and has the energy:

$$\langle E_6 \rangle = \langle \Phi_6 | H | \Phi_6 \rangle = \langle \sigma_u(1)\sigma_u(2) | h_1 + h_2 + h_{12} + \frac{1}{r_{AB}} | \sigma_u(1)\sigma_u(2) \rangle = 2h_u + J_{uu} + \frac{1}{r_{AB}}, \quad (12)$$

where  $J_{uu}$  is defined analogously to  $J_{gg}$ .

In order to estimate the energy of the states in question in the dissociation limit ( $r_{AB} \rightarrow \infty$ ), the energy formulae (7), (9), (11) and (12) are now presented in terms of the AOs. It is first found that:

$$h_g = \langle \sigma_g(\mu) | h_\mu | \sigma_g(\mu) \rangle = \frac{1}{2(1+S)} \langle s_A(\mu) + s_B(\mu) | h_\mu | s_A(\mu) + s_B(\mu) \rangle = \frac{1}{1+S} (h_{AA} + h_{AB}), \quad (13)$$

with

$$\begin{aligned} h_{AA} &\equiv \langle s_A(\mu) | h_\mu | s_A(\mu) \rangle = \langle s_B(\mu) | h_\mu | s_B(\mu) \rangle \equiv h_{BB}, \\ h_{AB} &\equiv \langle s_A(\mu) | h_\mu | s_B(\mu) \rangle \end{aligned} \quad (14)$$

and  $\mu$  taking the values 1 and 2. In the same way one obtains:

$$\begin{aligned}
 h_u &= \langle \sigma_u(\mu) | h_\mu | \sigma_u(\mu) \rangle = \frac{1}{1-S} (h_{AA} - h_{AB}), \\
 J_{gg} &= \frac{1}{2(1+S)^2} [J_{AA} + J_{AB} + 2K_{AB} + 4(AB\|AA)], \\
 J_{uu} &= \frac{1}{2(1-S)^2} [J_{AA} + J_{AB} + 2K_{AB} - 4(AB\|AA)], \\
 J_{gu} &= \frac{1}{2(1-S^2)} [J_{AA} + J_{AB} - 2K_{AB}], \\
 K_{gu} &= \frac{1}{2(1-S^2)} [J_{AA} - J_{AB}].
 \end{aligned} \tag{15}$$

In Eq. (15), the notation:

$$\begin{aligned}
 J_{AA} &\equiv \langle s_A(1)s_A(2) | h_{12} | s_A(1)s_A(2) \rangle = \langle s_B(1)s_B(2) | h_{12} | s_B(1)s_B(2) \rangle \equiv J_{BB}, \\
 J_{AB} &\equiv \langle s_A(1)s_B(2) | h_{12} | s_A(1)s_B(2) \rangle = J_{BA}, \\
 K_{AB} &\equiv \langle s_A(1)s_B(2) | h_{12} | s_B(1)s_A(2) \rangle = K_{BA}, \\
 (AB\|AA) &\equiv \langle s_A(1)s_B(2) | h_{12} | s_A(1)s_A(2) \rangle = (AB\|BB).
 \end{aligned} \tag{16}$$

is introduced.

At  $r_{AB} \rightarrow \infty$ , all the  $S$ ,  $h_{AB}$ ,  $J_{AB}$ ,  $K_{AB}$  and  $(AB\|BB)$  tend to zero, whereas  $J_{AA}$  takes the value denoted by  $J_{AA}^\infty$ ; consequently  $h_g$  and  $h_u$  become equal to the energy of an isolated hydrogen atom,  $E_H$ , and  $J_{gg}, J_{uu}, J_{gu}, K_{gu} \rightarrow J_{AA}^\infty / 2$ . Thus the dissociation limits of the energy formulae (7), (9), (11) and (12) are:

$$\begin{aligned}
 \langle E_1 \rangle^\infty &= 2E_H + \frac{1}{2} J_{AA}^\infty \equiv H_{11}^\infty ({}^1\Sigma_g^+), \\
 \langle E_{2,3,5} \rangle^\infty &= 2E_H \equiv E^\infty ({}^3\Sigma_u^+), \\
 \langle E_4 \rangle^\infty &= 2E_H + J_{AA}^\infty \equiv E^\infty ({}^1\Sigma_u^+), \\
 \langle E_6 \rangle^\infty &= 2E_H + \frac{1}{2} J_{AA}^\infty \equiv H_{66}^\infty ({}^1\Sigma_g^+).
 \end{aligned} \tag{17}$$

It can be seen that at  $r_{AB} \rightarrow \infty$ , the two states of the same spin and spatial symmetry,  ${}^1\Sigma_g^+$ , have the same energy, in contrast to the situation around the equilibrium geometry, where they are clearly separated from each other. Therefore, at very large internuclear distances, the interaction of these two species cannot be neglected. Thus, in order to obtain the correct dissociation channels for the states of  ${}^1\Sigma_g^+$  symmetry one has to apply the configuration interaction approach, *i.e.*, to solve the system of equations:



$$\begin{pmatrix} \langle \Phi_1 | H | \Phi_1 \rangle^\infty - E^\infty & \langle \Phi_1 | H | \Phi_6 \rangle^\infty \\ \langle \Phi_6 | H | \Phi_1 \rangle^\infty & \langle \Phi_6 | H | \Phi_6 \rangle^\infty - E^\infty \end{pmatrix} \begin{pmatrix} c_1^\infty \\ c_2^\infty \end{pmatrix} \equiv \begin{pmatrix} H_{11}^\infty - E & H_{16}^\infty \\ H_{16}^\infty & H_{66}^\infty - E \end{pmatrix} \begin{pmatrix} c_1^\infty \\ c_2^\infty \end{pmatrix} = 0, \quad (18)$$

where

$$\langle \Phi_1 | H | \Phi_6 \rangle^\infty = (J_{gu})^\infty = \frac{1}{2} J_{AA}^\infty. \quad (19)$$

One obtains:

$$\begin{aligned} E_1^\infty(^1\Sigma_g^+) &= H_{11}^\infty - H_{16}^\infty = 2E_H, \\ E_2^\infty(^1\Sigma_g^+) &= H_{11}^\infty + H_{16}^\infty = 2E_H + J_{AA}^\infty. \end{aligned} \quad (20)$$

Therefore, in the dissociation limit, the lower state of  $^1\Sigma_g^+$  symmetry runs into the same dissociation channel as the  $^3\Sigma_u^+$  species, while the  $^2^1\Sigma_g^+$  states dissociates into the same products as the  $^1^1\Sigma_u^+$  state.

Let us inspect the form of the approximate wave functions for the two  $^1\Sigma_g^+$  species considered. The spatial parts of the functions  $\Phi_1$  and  $\Phi_6$  are

$$\Phi_1: \quad \sigma_g(1)\sigma_g(2) = \frac{1}{2(1+S)} [s_A(1)s_B(2) + s_B(1)s_A(2) + s_A(1)s_A(2) + s_B(1)s_B(2)] \propto \Psi_{VB} + \Psi_{ion}, \quad (21)$$

$$\Phi_6: \quad \sigma_u(1)\sigma_u(2) = \frac{1}{2(1-S)} [-s_A(1)s_B(2) - s_B(1)s_A(2) + s_A(1)s_A(2) + s_B(1)s_B(2)] \propto -\Psi_{VB} + \Psi_{ion},$$

where

$$\begin{aligned} \Psi_{VB} &= N[s_A(1)s_B(2) + s_B(1)s_A(2)], \\ \Psi_{ion} &= N[s_A(1)s_A(2) + s_B(1)s_B(2)]. \end{aligned} \quad (22)$$

Thus, both of these wave functions correspond to the dissociation scheme according to which the dissociation into the ions ( $H^+ + H^-$ ) is equally probable as that into neutral atoms ( $H + H$ ), with the consequence that the energy of the dissociation channel is:

$$E^\infty(\Phi_1) = E^\infty(\Phi_6) = \frac{1}{2} [(E_H + E_H) + (E_{H^+} + E_{H^-})] = E_H + \frac{1}{2} E_{H^-}, \quad (23)$$

The wave functions corresponding to the asymptotic energies  $E_1^\infty(^1\Sigma_g^+)$  and  $E_2^\infty(^1\Sigma_g^+)$  are:

$$\begin{aligned} \Psi_1^\infty(^1\Sigma_g^+) &= \frac{1}{\sqrt{2}} (\Phi_1 - \Phi_6) = \frac{1}{\sqrt{2}} [s_A(1)s_B(2) + s_B(1)s_A(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)], \\ \Psi_2^\infty(^1\Sigma_g^+) &= \frac{1}{\sqrt{2}} (\Phi_1 + \Phi_6) = \frac{1}{\sqrt{2}} [s_A(1)s_A(2) + s_B(1)s_B(2)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]. \end{aligned} \quad (24)$$

The first of the wave functions (24) describes the dissociation of  $H_2$  into  $H + H$ , and the second one corresponds to the dissociation into the higher-energy channel involving  $H^+$  and  $H^-$  ions.

Thus, it can be concluded that the configuration interaction treatment (or some alternative approach which accounts for both the dynamic and non-dynamic correlation energy) is inevitable for the correct dissociative behavior of the ground electronic state of  $H_2$  to be obtained. In other words, the one-determinant approaches, such as HF or DFT, unavoidably lead to erroneous dissociation energy if it is computed as the difference between the asymptotic ( $r_{AB} \rightarrow \infty$ ) energy and the energy at the equilibrium geometry (see Fig. 1).

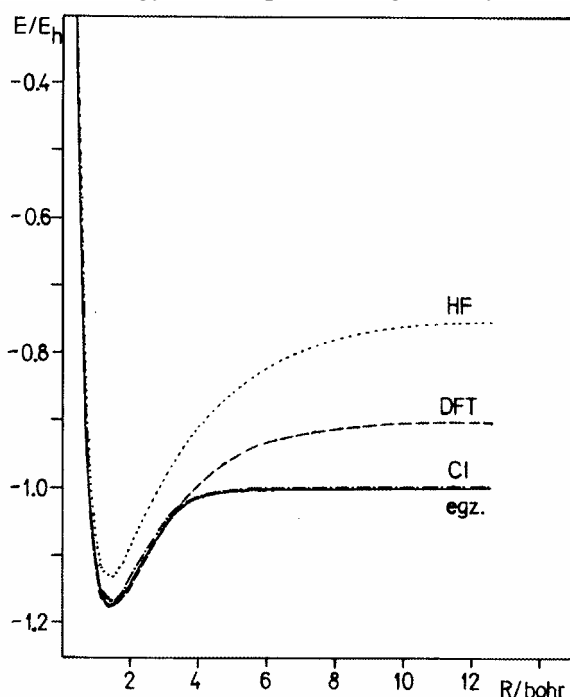


Fig.1. Potential energy curves for the  $H_2$  molecule computed by means of the HF, DFT and CI method and the exact potential energy curve as obtained by Kolos and Wolniewicz.<sup>6</sup>

### *Towards larger molecules*

In the two preceding subsections, some of the problems which arise by using compact program packages, such as Gaussian, for the calculation of molecular structure parameters were pointed out. There, as examples, only very small molecules built up of very light atoms and only the molecular (in majority of cases closed-shell) ground electronic states were considered as examples. When handling larger systems and/or excited electronic states, a number of additional problems have to be solved. Several of them will now be mentioned.

A typical quantum-mechanical task is to find the equilibrium geometry and the corresponding structure parameters of a large molecule (*i.e.*, a molecule composed of many atoms). The first problem which is encountered is the choice of the initial molecular geometry at which the calculation should commence. Theoretically, an *ab initio* quantum-mechanical approach does not require any infor-

mation about the molecule considered except of the number of its electrons and the number, the charges (and possibly masses) of its nuclei. However, in praxis some initial geometry has to be given. The program packages being considered normally incorporate some subroutines, such as *e.g.*, MOLDEN, which more or less automatically guess a reasonable initial geometry, but all the problems cannot be solved in this way. A molecule of say 100 atoms has a potential energy surface depending on 294 nuclear coordinates. It is to be expected that such a potential surface has a large number of local minima and the optimization of the molecular geometry is usually technically completed when one of these minima is attained. The local minimum which is found is to a great extent prejudiced by the choice of the initial geometry, *i.e.*, there is usually no guarantee that the global minimum of the potential surface, *i.e.*, the real equilibrium geometry, has been obtained. Another question is the physical/chemical meaning of local minima and the global minimum of a many-dimensional potential surface; how to interpret the results if there are several minima separated by very high or extremely low potential barriers?

Another difficult problem is the choice of the optimal approach and technical parameters (*e.g.*, AO bases, one-electron based functions in post-HF calculations, DFT functionals) for the system considered. As already mentioned, the HF and DFT approaches are usually not appropriate for calculating excited electronic states and the employment of methods accounting for the electron correlation more properly (Configuration Interaction, Coupled Cluster) is often not feasible for large molecules. Reliable computation of some structure parameters, such as hyperfine coupling constants, requires the use of special (typically compact) AO based functions; on the other hand, in the handling of negative ions and particularly a Rydberg electronic state, a standard AO basis must be augmented by several diffuse basis functions. By the choice of the method and the corresponding technical parameters, a fine balance between the desired accuracy of the final results and the computational requirements has to be achieved.

Special care is necessary when interpreting the obtained numbers. We mention only several questions which have to be answered: Does the computed property depend on the choice of the coordinate system (such as, *e.g.*, the dipole moment of an ion or the components of the hyperfine tensor)? Do the results depend on the choice of the subgroup of the actual point group of the molecule, employed in calculations? Why the components of a spatially degenerate electronic state of a linear molecule are sometimes computed to have different energy? Are the computed harmonic vibrational frequencies reliable? The answer to the last question necessitates knowledge of the manner in which the program computes them – by use of the second derivatives of the energy at equilibrium, energy gradients or in some other way. What is the reason for obtaining different values for two components of the bending vibrations in a spatially degenerate

electronic state of a linear molecule? Which results are physically/chemically justified and not simply artifacts?

#### CONCLUSIONS

The general conclusion which follows from the preceding analysis is that the employment of the available compact program packages for calculating molecular structure parameters and particularly the interpretation of results of such calculations requires a profound knowledge of chemistry, quantum mechanics, molecular dynamics and related topics. Although written by the experts in the field and accompanied with detailed manuals, these programs are by no means easy to handle. In order to obtain reliable results and to understand them, the user is often forced to obtain insight into the structure of the programs and underlying quantum-chemical methods, which cannot be learnt solely by studying the instructions for their use.

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#### ИЗВОД

#### ДА ЛИ СУ ПРОГРАМСКИ ПАКЕТИ ЗА РАЧУНАЊЕ СТРУКТУРЕ МОЛЕКУЛА ЗАИСТА “ЦРНЕ КУТИЈЕ”?

АНА МРАКОВИЋ, МИЛИЦА ДРВЕНЦИЈА, АЛЕКСАНДРА САМОЛОВ,  
МИЛЕНА ПЕТКОВИЋ и МИЉЕНКО ПЕРИЋ

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У овом раду показујемо да је широко распрострањено мишљење да се компактни програмски пакети за квантномеханичко рачунање структуре молекула могу безбрижно користити као “црне кутије” потпуно погрешно. Да бисмо то илустровали, приказујемо резултате рачунања дужине веза, вибрационих фреквенција и енергија дисоцијације за све хомонуклеарне двоатомске молекуле који укључују атоме из прве две периоде Периодног система, добијене помоћу програмског пакета Gaussian. Показано је да разумно коришћење програма претпоставља солидно познавање квантне хемије.

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