STUDY OF POTENTIAL CURVES BY UHF TYPE METHODS. POTENTIAL CURVE OF F_2 MOLECULE

Viliam KLIMO and Jozef TIŇO
Polymer Institute,
Slovak Academy of Sciences, 809 34 Bratislava

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The potential curve of the F_2 molecule was described with the use of the RHF, UHF, RMP2, UMP2, and PUHF methods and compared with the experimental one. Thus, the peculiarities of the various methods were revealed. The results suggest the direction of a further development of UHF type methods which would ensure a correct description of the given curve.

The study of potential curves of diatomic molecules with the aid of various quantum chemical approaches is the first step in seeking a method capable of yielding correct potential surfaces necessary to study the chemical reactivity of polyatomic molecules. The restricted Hartree–Fock method (RHF) usually fails in describing the dissociation limits of molecules, and the additionally applied limited configuration interaction or perturbation theory are not able to eliminate this disadvantage. Only the multiconfiguration approach (MC SCF) can ensure with the aid of a small number of determinants in the CI expansion a continuous dissociation process to products in their ground state. To this purpose, it is necessary to consider the electron configurations given in references[1,2] for certain homo- and heteronuclear diatomic molecules. These configurations, however, usually do not give a correct quantitative description of the potential curves and an additional CI or perturbation improvement of the MC SCF reference function is relatively difficult.

The study of the electron structure of molecular fluorine is important for the investigation of processes in the hydrogen fluoride and rare gas fluoride laser systems[3]. A correct reproduction of the potential curve of the F_2 molecule is also of importance for this purpose, however, it is rather difficult for the quantum chemical methods. The RHF wave function does not give the correct dissociation limit and, moreover, the energy for the equilibrium position of F_2 is higher than the two-fold RHF energy of the F atom (^2P) (the dissociation energy is negative in contrast to the experimental value). In addition, large changes of the correlation energy take place with the change of the internuclear distance[4]. The double-configuration wave function in the form

$$\Psi = c_1\{3\sigma_g^2 1\pi_u^4 1\pi_g^4\} + c_2\{3\sigma_u^2 1\pi_u^4 1\pi_g^4\},$$

in which the description of core orbitals $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2$ is suppressed, is the simplest MC SCF wave function which gives a qualitatively correct course of the potential curve for any internuclear distance. To obtain a quantitative agreement with the experimental curve, it is necessary either to increase the number of MC SCF configurations[5-7] or to carry out an extensive CI calculation[8] on the basis of molecular orbitals from the function Ψ. In the former case, Das and Wahl[5,6] calculated the dissociation energy $D_e = 1{\cdot}82$ eV with the use of a 6-configuration wave function. The latter involved excitations $3\sigma_g^2 \rightarrow 3\sigma_u^2$ and $1\pi_{u,g}^2 \rightarrow 3\sigma_u^2$, which are of the internal type, and excitations $3\sigma_g 1\pi_{u,g} \rightarrow 3\sigma_u 2\pi_{g,u}$ of the semi-internal type (terminology ac-

according to Hurley[9]). In the second case, Cartwright and Hay[8] optimized the orbitals and coefficients c_1, c_2 of the wave function Ψ by means of a generalized valence bond procedure, which is a sort of the MC SCF method. On the basis of these molecular orbitals, they performed the full CI calculation comprising 330—538 configurations for all internal and semi-internal excitations except for excitations from $1\sigma_g$ and $1\sigma_u$ orbitals. The value of $D_e = 1{\cdot}85$ eV thus obtained and the value of 1·82 eV according to Das and Wahl[6] exceed the experimental value of $1{\cdot}602 \pm 0{\cdot}006$ eV from the literature[10], possibly an evidence for lowering of the intra-atomic correlation energy in the forming process of the molecule. Taking into account external excitations of intra-atomic character[9], Das and Wahl[6] obtained the value of $D_e = 1{\cdot}67$ eV, which is together with other spectroscopic constants in good agreement with experiments.

In calculating the potential curve F_2, the double-configuration function Ψ was used also as a reference function for the application of Rayleigh–Schrödinger perturbation theory[11]. Already in the second order, this approach compensates the error of the single-determinant perturbation theory at larger internuclear distances. An expansion up to the fourth order neglecting the contributions from tri- and tetra-excitations gives a curve practically identical with the CI curve taking into account mono- and bi-excitations with respect to the same reference function.

It is seen from the mentioned example that even a qualitative description of dissociation of the F_2 molecule based on the RHF scheme requires a multideterminant function as reference for the perturbation theory. In UHF type calculations, a single-determinant function is generally sufficient for this purpose[12]. Since F_2 represents a special case (wrong sign of the dissociation energy), the aim of the present work is to study the peculiarities of the potential curves F_2 obtained by methods based on the UHF Slater determinant. In the first part of this series[12], we described the techniques of obtaining an SCF solution for the spin and space symmetry unrestricted Hartree–Fock method, which is able to reach smoothly the correct dissociation limit for most of the diatomic molecules. The second part[13] deals with the description of the potential curves of diatomic hydrides from the first group of the Mendeleev periodic system. A small basis set of gaussian orbitals is proposed, in which the UMP2 curves agree relatively well with experiments. In the present article, the peculiarities of the individual approaches are markedly manifested on the potential curve of the F_2 molecule. The RHF and RMP2 approaches fail in dissociation regions, the UHF and UMP2 approaches have disadvantages at equilibrium and mean internuclear distances. It is shown that a substantial improvement of the reference function is necessary to attain an accurate description; as an alternative, the involvement of higher orders in the UMP approach is proposed. The results suggest that the PUHF function could be a suitable reference function, the level of the second order of the perturbation theory being preserved.

CALCULATION METHODS AND BASIS SET

As mentioned in the introduction, a correct description of the dissociation limits with the use of a one-determinantal wave function requires to break the spin and space symmetry of the molecular orbitals from which the determinant is composed. The way of obtaining a correct SCF solution for such UHF method, which consists in the choice of a suitable starting function and in a dynamic selection of a damping parameter, was described in the first part ot this series[12] and is used also in the present paper. To remove the components of the UHF wave function with an undesirable spin multiplicity, the spin projection scheme according to Mestechkin and Whyman[14] was used. The PUHF method in this formulation is very advantageous for the spin projection after a variation of the UHF wave function for systems with any spin multiplicity. Correlation electron effects were also included on the basis of the perturbation theory according to Moller and Plesset[15] in the second order. This approach, based on the UHF reference function (UMP2 method), was used first in the work of Pople and coworkers[16]. We used besides for comparison the more common approach based on the RHF reference function (RMP2 method).

We used in our calculations a basis of gaussian functions, which is in spite of a relatively small number of basis functions suitable for the calculation of potential curves by the UMP2 method[13]. It is a minimum basis (*7s 3p*) with exponents and coefficients according to Roos and Siegbahn[17], augmented by six primitive gaussians centered at the middle of the bond. Of the bond functions, there are three gaussian *s*-functions with exponents 0·2, 0·7, and 3·0 plus a single set of *p*-functions with an exponent equal to 0·15.

RESULTS AND DISCUSSION

The potential curves calculated by the described methods are shown in Fig. 1. An experimental curve according to Lie and Clementi[1] serves for comparison; it is shifted upwards so as to agree with the RMP2 curve in the equilibrium distance.

The RHF wave function (as mentioned in the introduction) gives a wrong sing of the dissociation energy D_e^{RHF}, calculated with respect to the dissociation limit given as two-fold RHF energy of the F atom. This limit is in our approach identical with the supersystem limit, which is the same in the UHF, PUHF, and UMP2 methods (it is noted on the right border of Fig. 1) The value of D_e^{RHF} is in the presented basis equal to $-0{\cdot}79$ eV in comparison with $-2{\cdot}04$ eV (ref.[18]) in the basis of 7*s*, $4p_{x,y,z}$ functions on each F atom and in comparison with $-1{\cdot}37$ eV in the Hatree–Fock limit[19]. This suggests that the mentioned basis has a tendency to overestimate somewhat the bond effects.

The UHF curve shows that the F_2 molecule belongs to a small number of small closed shell systems[20,21] having a triplet instability in the region of equilibrium distances. As shown in preceding discussions[20-22], such a situation can occur in cases of a small energetic difference between the ground state and the lowest triplet state of the molecule. Calculations[8] give for the F_2 molecule a relatively small singlet-triplet separation of 3·32 eV in accord with the experimental estimate[23], 3·16 eV. The cited authors predicted an atypical minimum of the lowest triplet state for an internuclear distance of 0·19 nm. These facts elucidate somewhat the formation of an instability and the position of a minimum on the UHF curve in the region close to 0·22 nm. The point in which the UHF curve begins to deviate from the RHF solution is also interesting from the theoretical point of view. According to Mayer[24], in this point the first derivative of the UHF energy with respect to the distance is continuous (in contrast to the PUHF curve) and therefore the RHF and UHF curve must fluently deviate from each other. It can be said roughly that the

UHF curve corrects the wrong dissociation character of the RHF curve, but owing to an insufficient inclusion of the correlation effects it shows a shallow minimum shifted to larger internuclear distances.

To involve the correlation effects, a perturbation theory based on the RHF reference function is often used. This approach is disadvantageous since at larger internuclear distances a complete deformation of the curve is observed due to an unsuitable reference function, and this not only in the IEPA and CEPA methods[25] but also in the second and third order of the perturbation approach[11,26]. This is illustrated in Fig. 1, where the RMP2 curve attains a maximum at 0·25 nm and then abruptly decreases. It is interesting that this maximum is in other bases shifted to lower distances (about 0·15 nm (ref.[11]) and 0·23 nm (ref.[26]). Deformation of the curves after involving higher orders is observed already at smaller distances, probably owing to a divergence of the perturbation expansion[27].

At distances where the UHF curve becomes separated from the RHF curve, the UMP2 and RMP2 curves become also separated. Although the dissociation energy, $D_e^{\mathrm{UMP2}} = 1{\cdot}8$ eV, is in a rather good agreement with the experimental value of 1·602 eV (ref.[10]) and the UHF function is from the point of view of energy a better reference than the RHF function, the UMP2 curve is in the region of equilibrium and mean distances much deformed in comparison with the experimental one and is placed above the RMP2 curve. A similar deformation, but less mar ked and only in the region of medium distances was observed on the potential curves of hydrides[13]. A multiplet analysis showed in the case of the HF molecule[13] that the second order of the perturbation theory is not able to compensate the errors which the triplet component introduces into the UHF function. This effect takes place obviously

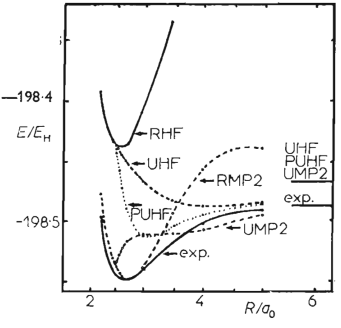

FIG. 1

Potential Curve for F_2 Molecule in Different Quantum Chemical Methods also in our work as evidenced by the PUHF curve, which is much different from the UHF curve. The whole course of the PUHF curve (although with considerable deviations from the experimental values of R_e and D_e) is relatively good and suggests that the PUHF wave function could become a good reference function for considering further correlation effects while preserving the second order of the perturbation theory. The question about the course of the potential curve in UMP approach including higher orders of the perturbation expansion remains open.

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