STUDY OF POTENTIAL CURVES BY UHF-TYPE METHODS. HOMONUCLEAR DIATOMICS OF SECOND ROW ATOMS

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Potential curves of Li_2, Be_2, B_2, C_2, and N_2 molecules in their ground states have been calculated in the minimal gaussian basis complemented by the bond functions. Comparison of results of the UHF, PUHF, and UMP2 methods with experimental curves shows that the UMP2 method gives qualitatively correct description of dissociation of all the studied molecules. For each of the molecules peculiarities of the potential curves are discussed from the point of view of their description by the UHF-type methods in the basis used.

When correlation effects are involved in quantum-chemical calculations, an important role is played by choice of a suitable reference function on the basis of which the CI or perturbation calculation is carried out. The unrestricted Hartree–Fock (UHF) function began to be used for this purpose only recently. The published works using the CI approach[1,2] or perturbation method[3–5] can serve as examples. As compared to the RHF approach, the UHF reference function has the advantage in its describing correctly the dissociation limits and, hence, giving possibility of consistent description of potential surfaces for any internuclear distances.

The problem of the UHF dissociation limits was discussed in the first communication of this series[6]. In the second part[7] a small basis set was suggested and used for a study of potential curves of hydrides of first row atoms. Correlation effects were involved on the basis of perturbation approach according to Moller–Plesser[8] in the 2. order constructed on the UHF reference function (the UMP2 method). The third part of this series[9] analyzed the peculiarities encountered in description of potential curve of F_2 molecule by means of the RHF- and UHF-type methods.

The present communication evaluates the possibilities of the UMP2 method in description of potential curves of homonuclear diatomics Li_2, Be_2, B_2, C_2, N_2 in ground states (the F_2 molecule was studied previously[9], and for a correct description of potential curve of O_2 molecule it is necessary to work with the generalized spin-orbitals[6,10]). The given series of molecules presents considerable difficulties with respect to quantum-chemical methods, because it provides a broad spectrum of bond types from the weak van der Waals molecule Be_2 to one of strongest chemical bonds in N_2 molecule. Therefore, each of the given molecules is treated separately.

Potential Curves

The calculations were carried out by the UHF method, its spin-projected version PUHF (ref.[11]) and UMP2. In the *ab initio* approach the minimal gaussian basis

set was used extended by six primitive gaussians located in the centre of the bond. The calculation algorithm and detailed description of the basis set are given in ref.[7]. Results of the calculations are given in Tables I – V and Figs 1 – 5.

The bond in Li_2 molecule (in ground state $^1\Sigma_g^+$), whose potential curves are given in Fig. 1 (1 eV = 1·6021 . 10^{-19} J, a_0 = 0·529177 . 10^{-10} m), belongs to chemical bonds of medium strength with dissociation energy D_e = 1·066 eV (ref.[12]). As compared with experimental curve[12] (which in this case and all the other figures is shifted to the common dissociation limit given in the right margin of the figures) the correction to the 2. order of perturbation theory improves but slightly the shape of the UHF curve (D_e^{UMP2} = 0·515 eV). Different shapes of the UHF and PUHF curves within the whole distance range indicate that the Li_2 molecule belongs to systems with triplet non-stability in the equilibrium distance where $\langle \mathbf{S}^2 \rangle_{UHF}$ = 0·68. This fact is connected with the existence of a low-lying triplet state[24]. For comparison, Fig. 1 also gives shape of the curve calculated on the basis of the linearized Coester–Kümmel theory[13,14] (LCKT) using the RHF reference function. For greater distances this method shows a divergence in the perturbation expansion, but in the equilibrium

TABLE I

The calculated potential curves of the Li_2 molecule (E/E_H)

R/a_0	E_{UHF}	E_{PUHF}	E_{UMP2}	E_{LCKT}
3·0	—14·7581	—14·7665	—14·7772	—14·7933
3·5	—14·7910	—14·7991	—14·8016	—14·8226
4·0	—14·8121	—14·8198	—14·8215	—
4·5	—14·8241	—14·8313	—14·8323	—14·8505
5·0	—14·8297	—14·8364	—14·8366	—
5·1	—14·8302	—14·8368	—14·8369	—14·8536
5·2	—14·8306	—14·8371	—14·8371	—14·8536
5·4	—14·8310	—14·8373	—14·8369	—14·8532
5·6	—14·8309	—14·8370	—14·8364	—14·8523
5·7	—14·8307	—14·8368	—14·8360	—14·8518
5·8	—14·8304	—14·8364	—14·8355	—14·8512
6·0	—14·8297	—14·8356	—14·8344	—14·8500
6·5	—14·8274	—14·8330	—14·8311	—14·8468
7·0	—14·8251	—14·8302	—14·8278	—14·8445
8·5	—14·8210	—14·8239	—14·8220	—
10·0	—14·8201	—14·8210	—14·8204	—
30·0	—14·8182	—14·8182	—14·8182	—

region the LCKT curve approaches to the experimental one. This fact indicates that the basis used is suitable for description of dissociation of Li_2, and that the previous methods do not sufficiently involve the correlation energy changes during this process.

For the van der Waals molecule Be_2 the experimental spectroscopic constants are not available. So far theoretical calculations considerably differ in their predictions.

TABLE II

The calculated potential curves of the Be_2 molecule (E/E_H)

R/a_0	E_{RHF}	$E_{RHF(CP)}$	E_{RMP2}	$E_{RMP2(CP)}$
4·7	—29·0666	—29·0596	—29·0866	—29·0797
5·0	—29·0702	—29·0647	—29·0884	—29·0828
5·25	—29·0720	—29·0672	—29·0886	—29·0838
5·5	—29·0731	—29·0689	—29·0883	—29·0841
5·75	—29·0740	—29·0702	—29·0879	—29·0840
6·0	—29·0748	—29·0711	—29·0874	—29·0837
7·0	—29·0776	—29·0737	—29·0861	—29·0822
8·0	—29·0796	—29·0754	—29·0850	—29·0808
8·5	—29·0801	—29·0759	—29·0842	—29·0801
9·0	—29·0802	—29·0763	—29·0834	—29·0794
20·0	—29·0769	—29·0769	—29·0769	—29·0769

TABLE III

The calculated potential curves of the B_2 molecule (E/E_H)

R/a_0	E_{UHF}	E_{PUHF}	E_{UMP2}
2·5	—49·0316	—49·0245	—49·0687
2·75	—49·0770	—49·0721	—49·1160
3·003	—49·0892	—49·0865	—49·1314
3·2	—49·0853	—49·0846	—49·1308
3·5	—49·0683	—49·0701	—49·1194
3·75	—49·0345	—49·0354	—49·1032
4·0	—49·0312	—49·0320	—49·0879
5·0	—49·0279	—49·0284	—49·0678
7·0	—49·0289	—49·0293	—49·0627
10·0	—49·0287	—49·0289	—49·0594
20·0	—49·0283	—49·0283	—49·0576

Lie and Clementi[15] obtained a repulsion potential curve. In a number of papers[16-18] an extrapolated dissociation energy D_e about 0·03 eV and an equilibrium distance about $4{\cdot}5 \cdot 10^{-10}$ m were accepted. On the basis of study of Be_2, Mg_2, Ca_2, Sr_2, Ba_2,

TABLE IV
The calculated potential curves of the C_2 molecule (E/E_H)

R/a_0	E_{UHF}	E_{PUHF}	E_{UMP2}
2·0	—75·3380	—75·3639	—75·4338
2·1	—75·3801	—75·4120	—75·4731
2·3474	—75·4216	—75·4644	—75·5019
2·5	—75·4218	—75·4660	—75·4939
2·7	—75·4081	—75·4486	—75·4721
3·0	—75·3748	—75·4063	—75·4325
3·5	—75·3255	—75·3460	—75·3761
4·0	—75·3121	—75·3222	—75·3518
5·0	—75·3129	—75·3156	—75·3417
7·0	—75·3151	—75·3162	—75·3367
10·0	—75·3140	—75·3144	—75·3320
20·0	—75·3127	—75·3127	—75·3296

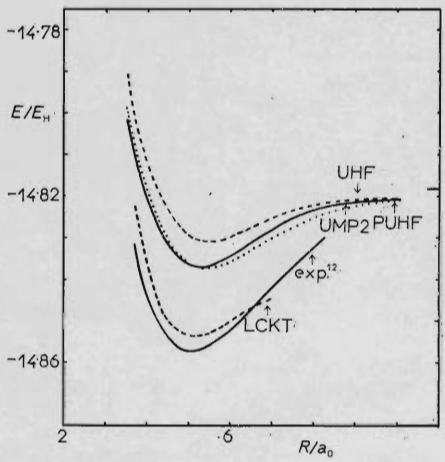

FIG. 1
Potential curves of the Li_2 molecule

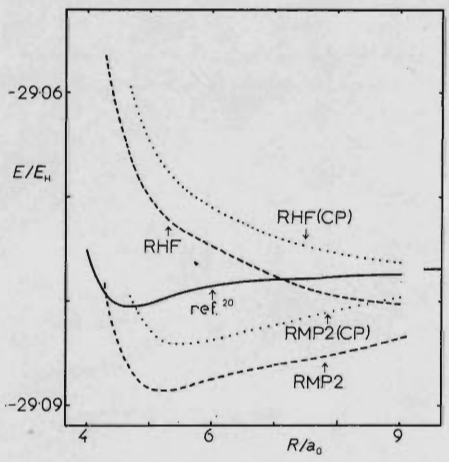

FIG. 2
Potential curves of the Be_2 molecule

and Ra_2 dimers Jones showed[19] that a simple extrapolation of D_e for Be_2 is incorrect, and he arrived at different values $D_e = 0{\cdot}35$ eV and $R_e = 2{\cdot}57 \cdot 10^{-10}$ m. The contemporary calculations by Liu and McLean[20], which exceed considerably the previous

TABLE V

The calculated potential curves of the N_2 molecule (E/E_H)

R/a_0	E_{UHF}	E_{PUHF}	E_{UMP2}
1·6	—108·3883	—108·3883	—108·5266
1·75	—108·6137	—108·6137	—108·7667
1·9	—108·7230	—108·7230	—108·8931
2·075	—108·7648	—108·7648	—108·9580
2·25	—108·7605	—108·7998	—108·9200
2·75	—108·7154	—108·7630	—108·8044
3·5	—108·6727	—108·6961	—108·7115
4·0	—108·6770	—108·6880	—108·7015
5·0	—108·6834	—108·6861	—108·6965
7·0	—108·6831	—108·6837	—108·6881
10·0	—108·6811	—108·6813	—108·6821
20·0	—108·6786	—108·6786	—108·6786

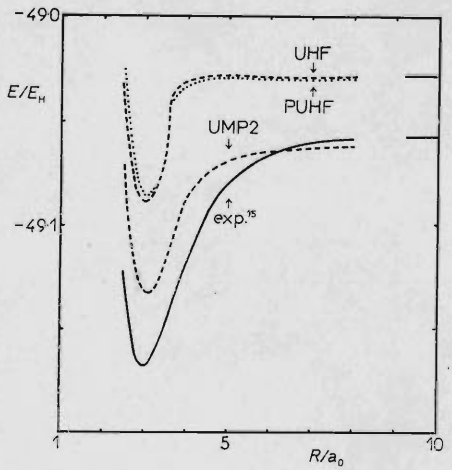

FIG. 3

Potential curves of the B_2 molecule

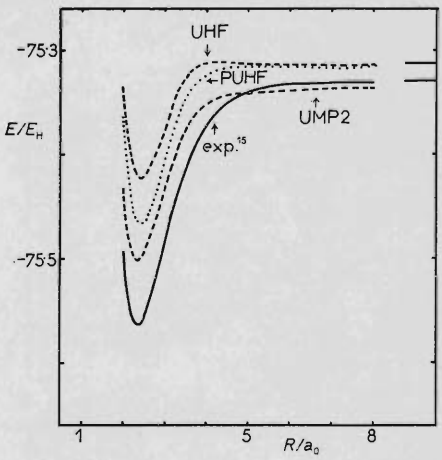

FIG. 4

Potential curves of the C_2 molecule

calculations with respect to magnitude of basis and extent of configuration interaction present authoritatively the values $D_e = 0{\cdot}10 \pm 0{\cdot}01$ eV and $R_e = (2{\cdot}49 \pm 0{\cdot}02) \cdot 10^{-10}$ m. In Fig. 2 the curves in our approach are presented. Within the whole range of internuclear distances no UHF solution was found different from the RHF one which shows a minimum at $4{\cdot}8 \cdot 10^{-10}$ m and a mild undulation at shorter distances. As studies of weak interactions use successfully the so called counterpoise correction for improving the defects of small bases (ref.[21]), we applied this correction at the RHF level – the curves RHF (CP) and RMP2 (CP). After this correction the undulation disappears, and the RHF (CP) curve assumes a repulsion character in accordance with the conclusion for the Hartree–Fock limit in ref.[20]. A similar effect is also manifested in the RMP2 curve, where the value $D_e^{RMP2} = 0{\cdot}32$ eV is improved to $D_e^{RMP2(CP)} = 0{\cdot}20$ eV. On the contrary, the equilibrium distance $R_e^{RMP2} = 2{\cdot}8 \cdot 10^{-10}$ m increases to $R_e^{RMP2(CP)} = 2{\cdot}9 \cdot 10^{-10}$ m. These results indicate that our approach can also be useful (after gathering more experience) for study of weak interactions.

The B_2 molecule has its ground state $^3\Sigma_g^-$. However, calculations by Dupuis and Liu[22] show that the quintet state is located relatively low, being even below the triplet curve for short internuclear distances. This phenomenon is also reflected in the relation between the UHF and PUHF curves in Fig. 3, where the spin projection in the triplet state increases energy at shorter internuclear distances (the spin contaminating quintet component lies lower). The overall shape of the UHF and PUHF curves is considerably deformed. Shape of the UMP2 curve is better as compared with the

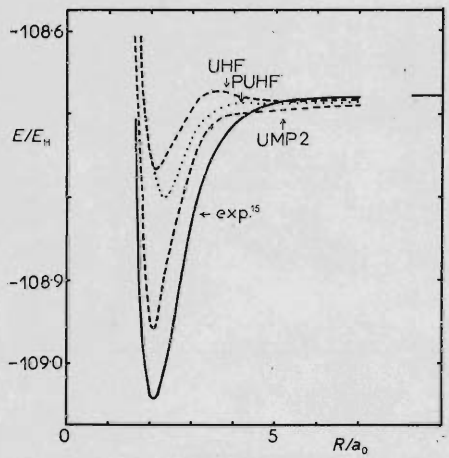

FIG. 5
Potential curves of the N_2 molecule

experimental curve[15], but the dissociation energy $D_e^{UMP2} = 2{\cdot}0$ eV is smaller than the experimental value 3·0 eV. In contrast to the above-mentioned molecules the dissociation limit of the UMP2 method is different from those of the UHF and PUHF methods. This fact is due to properties of our basis set in which, in the limit, the supersystem of atoms is treated in the minimal basis, and the atoms B and C only have unoccupied orbitals (see also Fig. 4) efficient from the point of view of the UMP2 description of correlation effects.

In case of the C_2 molecule ($^1\Sigma_g^+$ state) the UHF and PUHF curves differ in the whole distance range (Fig. 4). Kirby and Liu[23] showed that the molecule has several low-lying triplet states. It has already been mentioned that in such cases usually the triplet instability of the RHF treatment is maintained also for equilibrium distances. Occurrence of the maximum at the UHF curve at medium distances is completely removed only in the UMP2 method. The dissociation energy $D_e^{UMP2} = 4{\cdot}7$ eV, and the respective experimental value[23,24] is 6·23 eV.

Correct description of dissociation of triple bond in the N_2 molecule is one of the most difficult tasks of quantum chemistry. The concept of bond functions plays an important part therein[25], especially so in small bases, which is confirmed by our experience, too. Course of the UHF curve in Fig. 5 shows a maximum at medium distances, which is similar to the B_2 and C_2 molecules. Since the same maximum was also found by Bartlett and Purvis[26] for another type of basis, the matter is obviously in an imperfection of the UHF method. Although this imperfection is removed in the UMP2 method, the dissociation energy $D_e^{UMP2} = 7{\cdot}6$ eV is considerably underestimated as compared with the experimental value 9·91 eV. Contributions of the 3. and 4. order of the perturbation theory to the overall energy of the N_2 molecule calculated in the 6−31 G** basis[5] is about −0·5 eV, which indicates that the dissociation energy could be considerably improved in our basis by involving higher orders of the perturbation theory.

CONCLUSIONS

On the whole it can be stated that the UMP2 method in the given basis provides qualitatively correct description of dissociation of all the studied molecules. In the case of Be_2 molecule it was shown that the UMP2 method connected with our basis can be a useful means for study of weak interactions. In this case it is inevitable at the SCF level to take into account the superposition error resulting from the minimal basis and especially from bond functions. In description of dissociation of chemical bonds of medium and large strength by the UMP2 approach connected with the given basis the dissociation energy is underesimated especially in case of multiple bonds. A quantitative improvement can be expected from higher orders of the perturbation theory with the UHF reference function or from construction of perturbation theory on the spin-projected UHF or spin-extended Hartree–Fock reference function.

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