Energy Levels of F_2 and F_2^+†

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IF we calculate to the same degree of approximation the electronic energy levels of a molecule and of its ion, we are able (1) to obtain an extensive insight into the adiabatic potential curves, (2) to avoid arguments concerning physically meaningless results, and (3) to evaluate the ionization potential, the energies of the states in the Rydberg region, and other quantities having experimental importance.

Fluorine has the following characteristics as compared with the other second-row elements. The ratio of the atomic radius[1] to interatomic distance in diatomic fluorine is very small. In Table I this ratio is given for several diatomic molecules. We expect, therefore, that fluorine keeps its "atomic" character in the molecule. Especially, the effective nuclear charges (orbital exponents) in the molecule are not much different from those in the atom. This does not mean, however, that atomic methods are valid for this molecule. We discuss this point later. Secondly, all the excited levels of the fluorine atom are between 12.7 ev, $^2P(2s)^2(2p)^4(3s)$, and 17.4 ev, the ionization potential, above the ground state. Hence, to the ground state of F_2 the contribution from the higher configurations may be small. On the other hand, if we want to obtain some criterion of the accuracy of the calculated energy of higher excited states, we have to investigate the states of F_2^+. Here, the higher excited states and the higher configurations mean those which tend to the excited atomic structures at infinite separation of the atoms.

We took two interatomic distances and three different sets of effective nuclear charges and performed the ASMO treatment with configuration interactions. The configurations with $1s$ vacancies are not taken into account because of their negligible effects on the lower states. The $2s$ orbitals are orthogonalized to $1s$ in the form

$$N[r\exp(-\delta_2 r)+A\exp(-\delta_1 r)],$$

where δ_1 and δ_2 are the effective nuclear charges of the first and the second quantum orbitals.

The choice of δ_1 and δ_2 are made as follows: We varied δ_1 and δ_2 so as to minimize the total energy of the ground state (^2P) of atomic fluorine and determined $E=-98.941918$ a.u., $\delta_1=8.65$, and $\delta_2=2.56$. The change in E for the variation of δ_1 in the neighborhood of the minimum is much smaller than that for the variation of δ_2. Also, we did the same thing for all states of F^-, F, and F^+, and found that δ_1(minimum) changes only within the region 8.64–8.66 and that δ_2(minimum) in the states having the same ionicity are almost the same. Therefore, we fixed δ_1 as 8.65 and minimized the energies of all states of the atomic structures with respect to the variation of δ_2. Thus we found that the best δ_2 for the atomic structures F+F$^-$, F+F, and F+F$^+$ are 2.53, 2.56, and 2.62, respectively, regardless of the individual states. Therefore, the calculation was made for the following three sets of the effective nuclear charges:

	(a)	(b)	(c)
δ_1	8.65	8.65	8.65
δ_2	2.53	2.56	2.62

The ground state of F_2 is $^1\Sigma_g^+$ and 8 configurations having $2s$ and $2p$ deficiencies contribute to this state. Table II shows the dissociation energy and the equilibrium interatomic distance from the present calculation together with the results obtained previously. Rows (1) to (4) are based on the parameters shown in the first row. The present calculation is shown in (8). Since we took only two interatomic distances, the values of D_e and r_e in (1)–(4), (7), and (8) were determined by assuming a Morse curve:

$$U-D_e=D_e\{1-\exp[-\beta(r-r_e)]\}^2,$$

where β is related to the first vibrational frequency

TABLE I. Atomic radius/interatomic distance.

	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2
%	61	···	52	49	50	39	29

TABLE II. Dissociation energy and interatomic distance of F_2.

	D_e	r_e
1. Pilot calculation $\delta_1 R=20$ 25, $\delta_2 R=$ 6, 7.5, 8 configurations	2.04 ev	1.41 A
2. 6 configurations with s and σ deficiency	1.90	1.40
3. 4 configurations with σ and π deficiency	1.67	1.46
4. Shrinked $1s$ core, 8 configurations	2.63	1.31
5. In (4), $2s=(A+r)\exp(-\delta_2 r)$[a]	4.16	1.16
6. At the experimental r_e, LCAO SCF, 5 configurations[b]	1.96	···
7. Method of atoms in molecules	7.06	1.29
8. $\delta_1=8.65$		
(a) $\delta_2=2.53$	1.81	1.46
(b) $\delta_2=2.56$	1.99	1.44
(c) $\delta_2=2.62$	1.84	1.44
(d) Interpolated: $\delta_2=2.582$	2.02	···
9. Experiment	1.68	1.418

[a] Avraham Amith, thesis, Harvard University (in preparation).
[b] J. Eve, Proc. Roy. Soc. (London) **A246**, 582 (1958).

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[1] This atomic radius was given by J. C. Slater, Phys. Rev. **36**, 57 (1930), for the maximum radial density.

$\omega_e(=892.1\ \text{cm}^{-1})$

$$\beta \propto \omega_e(D_e)^{-\frac{1}{2}}.$$

Calculation (8d) was done by quadratic interpolation from (a), (b), and (c). In these, D_e's are obtained by subtracting the minimum total energy of the ground atomic structure which was shown previously. The value $\delta_2=2.582$ in the molecule is larger than the atomic δ_2, 2.56, as in other molecules. However, the difference is very small. In Li_2, for instance, this difference is about 0.10. Hence, by the variation of δ_2 from the best atomic value, the increase in D_e is much larger in Li_2 than in F_2. We note, furthermore, that in almost all cases, the calculation shows a higher dissociation energy than the experimental value, which is one of the remarkable features of the fluorine molecule calculation.

We have to mention how the method of atoms in molecules (MAM) does not show a good result as compared with ASMO treatments. The energy matrix in this method is expressed in the form

$$H(\text{MAM})=H(\text{ASMO})+\tfrac{1}{2}\{\tilde{T}(W-\bar{W})\tilde{T}^{-1}+T^{-1}(W-\bar{W})T\},$$

where T is the transformation matrix from the molecular wave functions to the normalized composite atomic functions, and W and $\bar{W}$ are the diagonal matrices of the experimental and the calculated atomic terms. The lowest configuration in the ground state tends to a valence state. The diagonal element of the lowest state calculated by MAM, therefore, differs by $-$ 0.18294 a.u. If we use the best effective nuclear charges for each state, this difference becomes -0.07740 a.u. This difference is always negative, since the calculation of the energy of the negative ion causes a largere error than for the states of other ionicities. Thus, in MAM the ground state is always calculated much lower than in ASMO.

We can, therefore, clearly fix our standpoint upon the ASMO method as far as the diatomic fluorine is concerned, and proceed with discussion on the excited states. In the lowest excited states we obtained a good agreement with experiment as shown in Table III. The energies are also calculated for several other states which adiabatically tend to the ground atomic structure. These states are all repulsive.

Since some discrete spectra were observed for F_2, we investigated higher states which tend to excited atomic structures at infinite separation. We calculated the difference of the energies of these states from the calculated values of the total energies of the adiabatic dissociation products, and by using the experimental atomic term values of these dissociation products, we located the energy levels. After the investigation of the lowest states of F_2^+, however, these states are found in the Rydberg region. Therefore, we cannot derive any physically significant results without taking into account the higher quantum orbitals.

TABLE III. Vertical excitation energy from (r_e).

	Calc	Exptl.
$^1\Pi_u$	4.49 ev	4.28 ev
$^3\Pi_u$	3.73	3.16
$^1\Pi_g$	6.50	···
$^3\Pi_g$	6.31	···

TABLE IV. Energy levels of the lowest states of F_2.

	$R=1.211\,A$	$R=1.514\,A$
$^2\Pi_g$	-3.161 ev	-4.026 ev
$^2\Pi_u$	2.446	-2.518
$^2\Sigma_u^+$	7.158	-0.023
$^2\Sigma_u^-$	10.347	3.515

The energies of $^2\Pi_g$, $^2\Pi_u$, $^2\Sigma_u^+$, and $^2\Sigma_u^-$ of F_2 are calculated in the same manner by using $\delta_1=8.65$ and $\delta_2=2.62$. In the calculation of F_2 we found that two states having the off-diagonal elements less than 0.05 a.u. do not appreciably affect each other in their energies. In each species, therefore, we took only those configurations which have off-diagonal elements larger than 0.05 with the lowest state. Thus, we obtained 7×7 secular equations for $^2\Pi_{g,u}$ and 2×2 for $^2\Sigma_u^{\pm}$. By solving these, results were obtained as shown in Table IV. These are the values from $F(^2P)+F(^3P)$, showing that three states are bonding. The calculation of F_2^+ is more refined if we take account of all the configurations and of the variation of the effective nuclear charges. If the calculation is refined in this manner, these states are lowered. Since there are no experimental data for F_2^+, the dissociation energy and the equilibrium distance cannot be determined. We can expect from this result, however, that r_e is much smaller and D_e is much larger than those of F_2.

Iczkowski and Margrave[2] measured Rydberg series of F_2 and determined the convergence limit at 15.7 ev above the GS $^1\Sigma_g^+$ at r_e. They also detected the ionic state $^1\Sigma_u^+$ at 11.96 ev above $^1\Sigma_g^+$ at r_e. Our calculation showed that the distances $^2\Pi_g-{}^1\Sigma_g^+(r_e)$ is 16.3 ev at 1.211 A and 15.4 ev at 1.54 A, and that $^1\Sigma_u^+-{}^1\Sigma_g^+(r_e)$ is 10.8 ev at 1.642 A. Here again, we used the experimental excitation and ionization energies of the atomic constituents and added to these the calculated differences between the atomic and molecular energies. With this rather artificial use of the experimental values, the results are not very absurd. Since the higher excited states of F_2 are apparently in the Rydberg region, the study of the Rydberg region will throw a new light on the theoretical treatment of molecular spectra.

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[2] R. P. Iczkowski and J. L. Margrave, J. Chem. Phys. **30**, 403 (1959).