Fourth-order MB RSPT calculations of the reaction energy and the equilibrium constant of the reaction $1/2 F_2 + 1/2 H_2 = HF$

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The many-body Rayleigh—Schrödinger perturbation theory (MB RSPT) truncated at the fourth order in energy, omitting triply excited configurations, is used to calculate potential energy curves and spectroscopic constants of F_2 , H_2 , and HF. Reaction heats and equilibrium constants of the gaseous phase reaction 1/2 $F_2 + 1/2$ $H_2 = HF$ are calculated for a series of temperatures. It is shown that the presented results are in a fairly good agreement with the experimental values.

Многочастичная теория возмущения Рэлея—Шредингера (МЧ ТВРШ) с ограничением четвертого порядка по энергиям и с исключением триплетно возбужденных конфигураций была использована для расчета кривых потенциальной энергии и спектроскопических констант молекул F_2 , H_2 и HF. Теплоты реакций и константы равновесий реакции в газовой фазе 1/2 $F_2 + 1/2$ $H_2 = HF$ были рассчитаны для ряда температур. Показано, что указанные результаты находятся в хорошем согласии с экспериментальными значениями.

In the last few years, the calculations of the correlation energy using MB RSPT of different levels of sophistication have found a wider range of applications. MB RSPT was successfully used for the calculations : of the equilibrium geometries of molecules [1, 2], of the force [3] and spectroscopic constants [4-7], in the study of chemical reactivity [8-11] and weak intermolecular interactions [12, 13].

In this work the above-mentioned method was applied to the study of the potential curves and associated spectroscopic constants of molecules F_2 , H_2 , HF. and also in the calculations of the reaction heats and the equilibrium constants of the reaction in which hydrogen fluoride is formed. This reaction is interesting for its very high exothermicity which is higher than the burning of molecular hydrogen in oxygen.

For a correct estimation of the reaction heat and equilibrium constant of the chemical reaction a consideration of the correlation energy is vital. Contributions to the correlation energy were calculated at several levels; the full second- and third-order, the fourth-order including singly-, doubly-, and quadruply-excited configurations as well as the simulated configuration interaction method with

singly- and doubly-excited configurations (CI-SD). We were forced to omit the triple excitations in the fourth order for great numerical difficulties connected with their calculation.

The aim of this work is also to discuss the quality of the rigid-rotor harmonic oscillator (RRHO) approximation in the calculation of the enthalpy and equilibrium constants of the reaction in comparison with the more sophisticated approximations which include the anharmonic corrections.

Calculations

The extended double zeta plus polarization basis set employed for calculations of F_2 , H_2 , and HF was a Gaussian (9s5p1d) basis set contracted to [4s3p1d] with all six possible d components included on fluorine [14] and (5s1p) set contracted to [3s1p] on hydrogen [15]. The hydrogen s-type functions were scaled by the factor 1.44. Exponents of the polarization functions were $\alpha_d = 1.4$ for fluorine [16] and $\alpha_p = 0.75$ for hydrogen.

For SCF calculations we used the POLYATOM/2 computer program [17] and SCF total energy converged at least to $10^{-8} E_{\rm H}$. The transformation of integrals over atomic orbitals to integrals over molecular orbitals as well as perturbation calculations of the correlation energy were performed using the POLYCOR [18] system of programs developed in our laboratory.

The spectroscopic constants: equilibrium distance, rotational constant, harmonic vibration frequency, anharmonicity constant, vibration-rotation interaction constant (R_e , B_e , ω_e , $\omega_e x_e$, α_e), were calculated in the case of the F₂ curve from the first 10 energy values, in the case of the H₂ curve from the first 13 energy values, and in the case of the HF curve from the first 12 energy values using the procedure of *Simons et al.* [19]. The difference between the known *Dunham* method [20, 21] and that mentioned above lies in the use of different expansion parameter, namely $(R - R_e)/R$ instead of $(R - R_e)/R_e$. The advantage of this modified procedure is its faster convergency. The total energy (*i.e.* E_{SCF}+ correlation correction) was expressed simply by a polynomial of the sixth degree. The method used seems to be quite sufficient [6].

The reaction heats and the equilibrium constants were calculated in two ways: a) the standard statistical thermodynamic treatment within the ideal gas plus **RRHO** approximation [22], b) the ideal gas approximation including corrections on anharmonicity and nonrigidity. The formulae were taken from JANAF Thermochemical Tables [23].

The spectroscopic constants as well as the equilibrium constants were computed by means of our own programs [24].

Results and discussion

Tables 1, 2, and 3 summarize the SCF energy and various correlation contributions of the investigated molecules. Double excitations in the second, third, and fourth order are denoted as $E_D^{(2)}$, $E_D^{(3)}$, and $E_D^{(4)}$. $E_S^{(4)}$ is the fourth-order contribution -

SCF energy and valence-shell correlation cor	ributions to the potential energy curves for F ₂
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R/a_0	$E_{ m scf}/E_{ m h}$	$E_{ m D}^{ m (2)}/E_{ m H}$	$E_{ m D}^{(3)}/E_{ m H}$	$E_{ m s}^{ m (4)}/E_{ m H}$	$E_{ m D}^{(4)}/E_{ m H}$	$E_{ m o}^{(4)}/E_{ m H}$	$E_{ extsf{r}}^{ extsf{(4)}}/E_{ extsf{h}}$	$E_{ m sdor}^{ m (4)}/E_{ m h}$
2.20	- 198.6986257	-0.40679	-0.00047	-0.00310	-0.00604	- 0.00690	0.01086	-0.00518
2.30	-198.7226882	-0.41304	0.00057	-0.00357	-0.00685	-0.00751	0.01201	-0.00593
2.40	-198.7353564	-0.41946	0.00162	-0.00410	-0.00779	-0.00815	0.01329	-0.00676
2.50	- 198.7396521	-0.42598	0.00266	-0.00469	-0.00888	-0.00880	0.01472	-0.00765
2.60	-198.7378456	-0.43256	0.00363	-0.00534	-0.01011	-0.00947	0.01631	-0.00861
2.68	- 198.7331868	-0.43785	0.00435	-0.00590	-0.01120	-0.01000	0.01769	-0.00941
2.80	-198.7224660	-0.44579	0.00526	-0.00680	-0.01304	-0.01079	0.01999	-0.01065
2.90	-198.7112460	0.45240	0.00586	-0.00761	-0.01477	-0.01145	0.02211	-0.01171
3.00	- 198.6987667	-0.45900	0.00629	-0.00846	-0.01668	-0.01209	0.02444	-0.01279
3.50	- 198.6317122	-0.49313	0.00578	-0.01328	-0.02952	-0.01518	0.04023	-0.01775
4.00	- 198.5717651	-0.53184	0.00087	-0.01902	-0.04996	-0.01839	0.06696	-0.02041
4.50	-198.5244603	-0.57673	-0.00889	-0.02576	-0.08099	-0.02191	0.11198	-0.01668
5.00	- 198.4888399	-0.62769	-0.02399	-0.03330	-0.12484	-0.02579	0.18463	0.00071

SCF energy and correlation contributions to the potential energy curves for H₂

R/a_0	$E_{ m scf}/E_{ m h}$	$E_{\scriptscriptstyle D}^{\scriptscriptstyle (2)}/E_{\scriptscriptstyle H}$	<i>Е</i> ⁽³⁾ / <i>Е</i> н	$E_{\rm s}^{(4)}/E_{ m H}$	<i>Е</i> ⁽⁴⁾ / <i>Е</i> н	E ⁽⁴⁾ /Ен	$E_{ m R}^{ m (4)}/E_{ m H}$	$E_{ m sdor}^{ m (4)}/E_{ m h}$
1.00	- 1.0833668	-0.02718	-0.00543	-0.00003	-0.00134	0.00000	0.00020	-0.00117
1.10	-1.1089013	-0.02728	-0.00552	-0.00004	-0.00141	0.00000	0.00021	-0.00123
1.20	-1.1236507	-0.02742	-0.00564	-0.00005	-0.00149	0.00000	0.00022	-0.00132
1.30	-1.1307795	-0.02761	-0.00578	-0.00007	-0.00158	0.00000	0.00024	-0.00141
1.35	-1.1321946	-0.02772	-0.00586	-0.00007	-0.00164	0.00000	0.00024	-0.00147
1.40	-1.1324649	-0.02784	-0.00595	-0.00008	-0.00170	0.00000	0.00025	-0.00153
1.45	-1.1317641	-0.02796	-0.00604	-0.00009	-0.00176	0.00000	0.00026	-0.00159
1.50	-1.1302394	-0.02810	-0.00613	-0.00010	-0.00182	0.00000	0.00027	-0.00166
1.60	-1.1252015	-0.02839	-0.00634	-0.00013	-0.00197	0.00000	0.00029	-0.00181
1.70	-1.1181496	-0.02872	-0.00657	-0.00016	-0.00214	0.00000	0.00031	-0.00198
1.90	-1.1002017	-0.02951	-0.00713	-0.00022	-0.00254	0.00000	0.00037	-0.00240
2.10	-1.0795138	-0.03049	-0.00781	-0.00031	-0.00305	0.00000	0.00044	-0.00292
2.50	-1.0361984	-0.03321	-0.00969	-0.00055	-0.00450	0.00000	0.00065	-0.00440
3.00	-0.9853458	-0.03824	-0.01320	-0.00100	-0.00733	0.00000	0.00113	-0.00720
4.00	-0.9043675	-0.05488	-0.02532	-0.00260	-0.01786	0.00000	0.00367	-0.01678
5.00	-0.8483358	-0.08108	-0.04594	-0.00538	-0.03747	0.00000	0.01138	-0.03147
6.00	-0.8106065	-0.11589	-0.07598	-0.00936	-0.06850	0.00000	0.03089	-0.04697

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Table 3

R /a ₀	$E_{ m scf}/E_{ m h}$	$E_{ m D}^{(2)}/E_{ m H}$	$E_{\scriptscriptstyle m D}^{ m (3)}/E_{\scriptscriptstyle m H}$	$E_{ m s}^{ m (4)}/E_{ m H}$	$E_{ m D}^{(4)}/E_{ m H}$	$E_{ m o}^{(4)}/E_{ m H}$	$E_{ m R}^{ m (4)}/E_{ m H}$	$E_{ m sdor}^{ m (4)}/E_{ m H}$
1.30	- 99.9471750	-0.21310	-0.00143	-0.00102	-0.00213	-0.00287	0.00392	-0.00209
1.40	-100.0001164	-0.21592	-0.00093	-0.00110	-0.00230	-0.00304	0.00412	-0.00232
1.50	- 100.0303645	-0.21867	-0.00039	-0.00119	-0.00249	-0.00322	0.00432	-0.00258
1.60	-100.0450646	-0.22133	0.00016	-0.00131	-0.00270	-0.00342	0.00455	-0.00288
1.70	-100.0491071	-0.22394	0.00072	-0.00144	-0.00293	-0.00363	0.00480	-0.00320
1.73	-100.0487760	-0.22471	0.00089	-0.00148	-0.00300	-0.00369	0.00487	-0.00330
1.80	-100.0458637	-0.22650	0.00128	-0.00159	-0.00318	-0.00384	0.00506	-0.00355
1.90	-100.0376820	-0.22901	0.00182	-0.00175	-0.00346	-0.00405	0.00534	-0.00392
2.10	-100.0126262	-0.23389	0.00286	-0.00213	-0.00411	-0.00448	0.00596	-0.00476
2.30	- 99.9821740	-0.23868	0.00380	-0.00260	-0.00487	-0.00490	0.00667	-0.00570
2.50	- 99.9504442	-0.24344	0.00463	-0.00318	-0.00576	-0.00533	0.00750	-0.00678
3.00	- 99.8763427	-0.25582	0.00622	-0.00541	-0.00869	-0.00635	0.01023	-0.01022
4.00	- 99.7672885	-0.28564	0.00818	-0.01798	-0.01790	-0.00843	0.02106	-0.02325
5.00	- 99.6998991	-0.32534	0.01129	-0.06129	-0.03247	-0.01075	0.04727	-0.05725

from single excitations. $E_Q^{(4)}$ represents the net contribution to the correlation energy due to quadruple excitations in the fourth order. $E_R^{(4)}$ is the fourth-order renormalization term. $E_{SDQR}^{(4)}$ is a sum of the following terms: $E_S^{(4)}$, $E_D^{(4)}$, $E_Q^{(4)}$, and $E_R^{(4)}$. All the energy contributions are thoroughly discussed elsewhere [25, 26].

It can be seen that the double excitations represent the most important contribution to the correlation attraction. The dominant part of the effect is already obtained at the second order.

The resulting potential curves of F₂, H₂, and HF are presented in Figs. 1—3 and the corresponding spectroscopic constants are in Tables 4—6. The notation for figures and tables is as follows: $E^2 = E_{SCF} + D_D^{(2)}$, $E^3 = E^2 + E_D^{(3)}$, $E^4 = E^3 + E_{SDQR}^{(4)}$, $E_{CI-SD}^{(2)-(4)}$ is the fourth-order approximation to CI-SD, $E_{CI-SD}^{(2)-(4)} = E_D^{(2)} + E_D^{(3)} + E_D^{(4)} + E_S^{(4)} + E_R^{(4)}$.

We can see that the inclusion of the correlation energy contributions widens the potential energy curves in comparison to SCF results and leads to improved prediction of vibration frequencies. The unphysical behaviour of the potential energy curves for large interatomic distances is apparent from the figures. This reflects a well known fact that the one-determinant wave function is quite



Fig. 1. Potential energy curves for the ground state of the fluorine molecule.

Fig. 2. Potential energy curves for the ground state of the hydrogen molecule.



Fig. 3. Potential energy curves for the ground state of the hydrogen fluoride.

insufficient for the description of the dissociated systems. Also connected with this is a poor convergency of the perturbation expansion for large distances. For example, let us take the hydrogen molecule at a distance of $6 a_0$. The energy contributions due to double excitations in the second through the sixth order are as follows: -0.11589, -0.07598, -0.06850, -0.06157, $-0.05553 E_{\rm H}$.

Ta	ble	4

	S	pectroscopic co	nstants of F_2		
	$R_{e}/10 \text{ m}^{-1}$	B_{e}/cm^{-1}	$\omega_{e}/\mathrm{cm}^{-1}$	$\omega_{\rm e} x_{\rm e}/{\rm cm}^{-1}$	$\alpha_{e}/\mathrm{cm}^{-1}$
SCF	1.331	1.00	1266	7.4	0.008
2nd order	1.408	0.90	983	9.9	0.011
3rd order	1.395	0.91	1011	10.5	0.011
4th order (SDQR)	1.410	0.89	952	11.8	0.012
CI-SD ⁽²⁾⁻⁽⁴⁾	1.379	0.93	1078	9.2	0.010
Exp. [28]	1.412	0.89	917	11.2	0.014

1	a	b	e	5

	$R_{e}/10 \text{ m}^{-1}$	B_{e}/cm^{-1}	$\omega_{c}/\mathrm{cm}^{-1}$	$\omega_e x_e/\mathrm{cm}^{-1}$	a_{e}/cm^{-1}		
SCF	0.734	62.0	4599	104.7	2.612		
2nd order	0.738	61.5	4532	106.8	2.673		
3rd order	0.740	61.1	4484	108.6	2.722		
4th order	0.742	60.8	4447	109.4	2.770		
Exp. [23]	0.742	60.8	4405	125.3	3.066		

Spectroscopic constants of H

Table 6

	$R_{e}/10 \text{ m}^{-1}$	$B_{\rm c}/{\rm cm}^{-1}$	$\omega_{e}/\mathrm{cm}^{-1}$	$\omega_{e} x_{e}/\mathrm{cm}^{-1}$	$\alpha_{e}/\mathrm{cm}^{-1}$
SCF	0.899	21.8	4468	84.6	0.748
2nd order	0.919	20.8	4168	86.3	0.768
3rd order	0.915	21.1	4237	86.6	0.767
4th order (SDQR)	0.918	20.9	4183	87.9	0.778
CI-SD ⁽²⁾⁻⁽⁴⁾	0.914	21.1	4243	86.9	0.769
Exp. [23]	0.917	21.0	4138	89.9	0.798

Spectroscopic constants of HF

It is evident that in the case of the hydrogen molecule $E_{\text{SDOR}}^{(4)}$ represent the full fourth-order contribution, which is identical with the fourth-order approximation to full CI.

As can be seen from Tables 4—6 the correlation corrections of the SCF values considerably improve agreement of all the spectroscopic constants, and therefore MB RSPT correctly describes the potential energy curve in the region of the minimum in contradistinction to the region of large distances. The quality of the second-order values of spectroscopic constants is remarkable [4—7].

 ΔE of the reaction considered, obtained from SCF energies of the investigated molecules calculated in experimental geometries led to the value -304.4 kJ mol⁻¹. For this reaction the estimated Hartree—Fock limit is -299.8 ± 4.8 kJ mol⁻¹ [27], so that at least at the SCF level the basis set seems to be reliable. We now comment on Tables 7 and 8, which show collected values of ΔH^0 and log K of the title reaction for the series of temperatures. From Table 7 we can see that there are very small differences between values obtained by means of the RRHO approximation and by using the more sophisticated method. Within the accuracy the values of log K presented in Table 8 are indistinguishable by these two methods. CI-SD

			Table 7. 4	ΔH^{o}_{T} (kJ mo	d^{-1}) of the r	eaction $\frac{1}{2}$ F ₂	$_{2} + \frac{1}{2} H_{2} = H_{2}$	F			
Т/К		0	298	500	1000	1500	2000	3000	4000	5000	6000
SCF	a	- 287.5	- 287.5	-287.7	- 288.9	- 290.2	-291.4	-292.8	- 293.7	- 294.3	- 294.6
	b	- 287.6	- 287.6	-287.8	- 289.0	- 290.5	-291.6	-293.3	- 294.4	- 295.3	- 296.1
2nd order	a	-274.6	-274.6	-274.9	-276.4	-277.7	-278.7	-280.0	- 280.7	-281.1	-281.4
	b	-274.7	-274.7	-275.0	-276.6	-278.0	-279.2	-280.8	- 282.1	-283.2	-284.4
3rd order	a	- 269.3	-269.3	- 269.6	-271.0	-272.5	-273.5	- 274.9	-275.6	-276.1	-276.4
	b	- 269.4	-269.4	- 269.7	-271.2	-272.8	-274.0	- 275.7	-277.1	-278.4	-279.7
4th order (SDQR)	a	-264.1	-264.1	-264.4	-265.9	- 267.3	- 268.3	- 269.7	-270.4	- 270.9	-271.2
	b	-264.1	-264.2	-264.5	-266.1	- 267.7	- 268.9	- 270.7	-272.2	- 273.7	-275.2
CI-SD ^{(2)—(4)}	a	-287.3	-287.3	-287.6	-289.0	- 290.4	-291.4	- 292.8	- 293.5	- 294.0	- 294.4
	b	-287.4	-287.4	-287.7	-289.1	- 290.6	-291.8	- 293.5	- 294.7	- 295.8	- 296.9
Exp. [23]		-272.5	-272.5	-272.9	-274.6	-276.2	-277.6	-279.9	- 282.3	-285.0	-288.2

a) RRHO approximation; b) approximation including corrections on anharmonicity and nonrigidity.

					2 L				
<i>T/</i> K	298	500	1000	1500	2000	3000	4000	5000	6000
SCF	50.8	30.4	15.4	10.3	7.8	5.3	4.0	3.2	2.7
2nd order	48.5	29.1	14.7	9.8	7.4	5.0	3.8	3.0	2.5
3rd order	47.6	28.5	14.4	9.7	7.3	4.9	3.7	3.0	2.5
4th order (SDQR)	46.7	30.0	14.1	9.5	7.1	4.8	3.6	2.9	2.4
CI-SD ⁽²⁾⁻⁽⁴⁾	50.8	30.4	15.4	10.3	7.8	5.2	3.9	3.2	2.7
Exp. [23]	48.1	28.8	14.5	9.7	7.3	4.9	3.7	3.0	2.5

Table 8. log K of the reaction $\frac{1}{2}$ F₂ + $\frac{1}{2}$ H₂ = HF

results are very similar to SCF results. To our sorrow the most sophisticated approach E^4 led to 8 kJ mol⁻¹ error for ΔH_0^0 . This error could have been accounted for by the absence of triple excitations, which in some reactions may be quite important [29], however very recent calculations of triple excitations give for F₂ and HF in experimental geometries the values -0.01367 and $-0.00444 E_h$ [30]. This increases that error to 14 kJ mol⁻¹. So it is evident that the correlation level is more sensitive to quality of basis set than the SCF level. In order to obtain results within the chemical accuracy it is desirable to choose a larger basis set than DZ + P and perhaps also inclusion of f functions would be necessary [31]. The best results, within the chemical accuracy, were obtained at the second order. This very good behaviour of the second order must be taken as a fortuitous cancellation of small errors and cannot be entirely generalized. In reaction with negative ions NH₂⁻ + H₂ = NH₃ + H⁻, the third-order contribution proved to be very important [32], so that some caution in using the second order alone is necessary.

In conclusion, we present a short summary of what in our opinion seems to be the most rational way of evaluation of the equilibrium constants of chemical reactions, at least of those which are under enthalpic control:

- i) basis set of the DZ + P or better quality,
- ii) using the RRHO approximation,
- iii) calculation of ω_e by means of the second-order MB RSPT,

iv) calculation of ΔE using the best possible approach which includes correlation energy.

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