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Fourth-Order MB-RSPT Calculations of the Spectroscopic Constants and Potential Energy Curve of F_2

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The spectroscopic constants and the potential energy curve of F_2 were calculated, using the fourth-order MB-RSPT with a single-determinant RHF starting wave function. With an extended [5s4p2d1f] basis set we obtained the equilibrium bond distance and the harmonic vibrational frequency with a relative error of about 0.5%, these are in very good agreement with experiment. In calculations of the potential energy curve for distances larger than about 1.4 R_e the method breaks down. We analysed the effect of the individual fourth-order contributions: single, double, triple and quadruple excitations. The role of the renormalization term was stressed in the discussion of various approximations to the full fourth-order energy and in comparison with other related approaches. The basis set effect has been also examined.

Key words: MB-RSPT – F_2 – Spectroscopic constants – Potential energy curve – Basis set effect.

1. Introduction

The Many-Body Rayleigh–Schrödinger Perturbation Theory (MB-RSPT) is presently well established as a powerful alternative method for investigation of the correlation problem in *ab initio* calculations of molecular systems. The present

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state-of-art of this approach, its advantages, limitations and applications has been reviewed recently by Bartlett [1].

The most sophisticated level of MB-RSPT, still applicable to moderately large molecules, is represented by the full fourth-order energy [2–13]. The applications of this method to chemical problems are still very scarce [4, 10–13], so that any further information on its reliability may be useful. In this paper we tried to examine the behaviour of the fourth-order MB-RSPT in calculation of potential energy curves of diatomic molecules using F_2 as a model system. We were interested in the reliability of MB-RSPT in the vicinity of the equilibrium distance (this reliability may be estimated by calculations of spectroscopic constants), where the single determinant MB-RSPT is expected to work well, as well as in the question, how far from equilibrium is the method still applicable. The correct answer to this last question is important in using such an approach for calculations of potential hypersurfaces in chemical reactions and particularly in predictions of geometry and energy of transition states. Unfortunately in bond breaking processes we must expect difficulties for larger interatomic distances due to problems with quasi-degeneracy.

In our work we proceeded in two steps. Our first aim was to analyse individual fourth-order contributions (single, double, triple and quadruple excitations) and their importance in calculating the spectroscopic constants and potential energy curve of F_2 and to compare the results at various levels of approximation to the full fourth-order with the ones obtained using other related approaches, namely CEPA [14, 15] and CPMET [15]. In this step we have used the moderately large [4s3p1d] Gaussian basis set. In the second step we have used a very extended [5s4p2d1f] basis set. In this step we were interested mainly in the question of how accurate the full fourth-order spectroscopic constants (calculated with a presumably saturated basis set) are in comparison with experiment. Moreover, our results offer the possibility to compare the spectroscopic constants obtained by the single determinant fourth-order MB-RSPT with those obtained by Blomberg and Siegbahn [16] who used exactly the same basis with the multi-configuration MC-SCF-CI method.

2. Computational Method

The computational aspects of the fourth-order MB-RSPT as well as its relation to other methods have been described elsewhere [1–3, 8, 17–27] and need not be repeated here in detail. It is just useful to mention that the total contribution from the connected fourth-order quadruple-excitation diagrams, $E^{(4)}_{QR}$, will in our paper be separated [19, 20] into two terms, i.e. $E^{(4)}_{QR} = E^{(4)}_{Q} + E^{(4)}_{R}$. They represent the net effect of quadruple-excitations and the uncancelled part of the renormalization term, respectively. $E^{(4)}_{Q}$ is represented by disjoint (DJ) terms of connected quadruple-excitation diagrams, while $E^{(4)}_{R}$ is given as the conjoint (CJ) part* of the fourth-order renormalization term $[-E^{(2)}_{D}S]_{CJ}$. In $-E^{(2)}_{D}S$, $E^{(2)}_{D}$

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* An alternative terminology for terms "conjoint" and "disjoint" is "EPV", i.e. exclusion principle violating and "non-EPV", which is most often used, but is not quite correct [8, 27].

denotes the energy of second-order double excitations and S is the renormalization factor of the first-order wave function. In methods which are not size-extensive, e.g. configuration interaction restricted to double excitations (CI-D), the complete $-E_{\mathrm{D}}^{(2)}S$ contributions remains uncancelled.

Although the above mentioned separation of $E_{\mathrm{QR}}^{(4)}$ into $E_{\mathrm{Q}}^{(4)}$ and $E_{\mathrm{R}}^{(4)}$ is not invariant to unitary transformation from canonical to localized orbitals, it is suitable in discussion of the relation of MB-RSPT to other approaches.

Other MB-RSPT contributions to the correlation energy are $E_{\mathrm{D}}^{(3)}$, $E_{\mathrm{D}}^{(4)}$, etc., i.e. third-order, fourth-order, etc., contributions from double-excitations and $E_{\mathrm{S}}^{(4)}$, $E_{\mathrm{T}}^{(4)}$, i.e. fourth-order contributions from single and triple-excitations. Total correlation energy up to the fourth order is then $E_{\mathrm{SDTQR}}^{(2)-(4)} = E_{\mathrm{D}}^{(2)} + E_{\mathrm{D}}^{(3)} + E_{\mathrm{D}}^{(4)} + E_{\mathrm{S}}^{(4)} + E_{\mathrm{T}}^{(4)} + E_{\mathrm{QR}}^{(4)}$. As an approximation of CI-D up to the fourth order we use the expression $E_{\mathrm{CI\text{-}D}}^{(2)-(4)} = E_{\mathrm{D}}^{(2)-(4)} + [-E_{\mathrm{D}}^{(2)}S]$, which is not size-extensive, in contrast to $E_{\mathrm{D}}^{(2)-(4)} + E_{\mathrm{R}}^{(4)}$, which is a correct (size-extensive) representation of double-excitations. Notation for other contributions in complete fourth-order energies is obvious.

Spectroscopic constants were obtained by the same procedure as before [28] using the modified Dunham method [29, 30]. The total energy (SCF + correlation energy) was fitted by a polynomial of degree six. Energy points, which correspond to distances outside the maximum of the potential curves were excluded from the fit.

As we have already mentioned, two different basis sets were used. The smaller one was a Gaussian (9s5p1d) set [31] contracted [32] to [4s3p1d], with exponents of six d-functions $\alpha_d = 1.4$ [14]. A very similar basis set has been used in CEPA and CPMET calculations [14, 15]. The extended basis set was a (10s6p2d1f) Gaussian set [31] contracted [33] to [5s4p2d1f], with polarization functions taken from Ref. [14]. It is identical to that used by Blomberg and Siegbahn [16] in their MC-SCF-CI calculations.

Calculations with a [4s3p1d] set were performed in Bratislava on a SIEMENS 4004 computer using the POLYATOM/2 program [34] for the SCF part and the POLYCOR program [21, 35] (developed in our laboratory) for transformation of integrals and MB-RSPT calculations. Results with a [5s4p2d1f] basis set were obtained in Garching on a AMDAHL 470 V/6 computer using the MUNICH system of programs [36] for SCF and transformation parts and POLYCOR for MB-RSPT calculations.

3. Results

The energy calculations which will be used in the forthcoming discussion are collected in Tables 1 and 2. Some additional energy components with [4s3p1d] basis may be found in our previous work [37]. Spectroscopic constants are shown in Tables 3 and 4. The potential energy curves obtained with various approaches are presented in Fig. 1 for basis [4s3p1d] and in Fig. 2 for the extended basis.

Table 1. SCF energy (in (E/E_h)) and valence-shell correlation contributions (in $10^3\,E/E_h$) of F_2 at various internuclear distances (in R/a_0). [4s3p1d] basis

R	$-E_{SCF}$	$-E^{(2)-(4)}_{SDTQR}$	$-E^{(2)-(4)}_{D}$	$-E^{(4)}_{S}$	$-E^{(4)}_{T}$	$-E^{(4)}_{Q}$	$E^{(4)}_{R}$	$-E^{(2)}_{D}S$
2.20	198.6986257	421.56	413.30	3.10	9.12	6.90	10.86	30.24
2.30	198.7226882	428.36	419.32	3.57	9.95	7.51	12.01	32.51
2.40	198.7353564	435.44	425.63	4.10	10.85	8.15	13.29	35.02
2.50	198.7396521	442.79	432.20	4.69	11.81	8.80	14.72	37.79
2.60	198.7378456	450.36	439.04	5.34	12.82	9.47	16.31	40.82
2.68	198.7331868	456.58	444.70	5.90	13.67	10.00	17.69	43.44
2.80	198.7224660	466.20	453.57	6.80	15.02	10.79	19.99	47.71
2.90	198.7112460	474.46	461.31	7.61	16.21	11.45	22.11	51.61
3.00	198.6987668	482.95	469.39	8.46	17.46	12.09	24.44	55.84
3.50	198.6317122	529.95	516.87	13.28	24.85	15.18	40.23	83.23
4.00	198.5717651	586.27	580.93	19.02	34.90	18.39	66.96	126.45
4.50	198.5244603	650.82	666.61	25.76	48.52	21.91	111.98	194.88
5.00	198.4888399	717.35	776.52	33.30	66.39	25.79	184.63	299.59

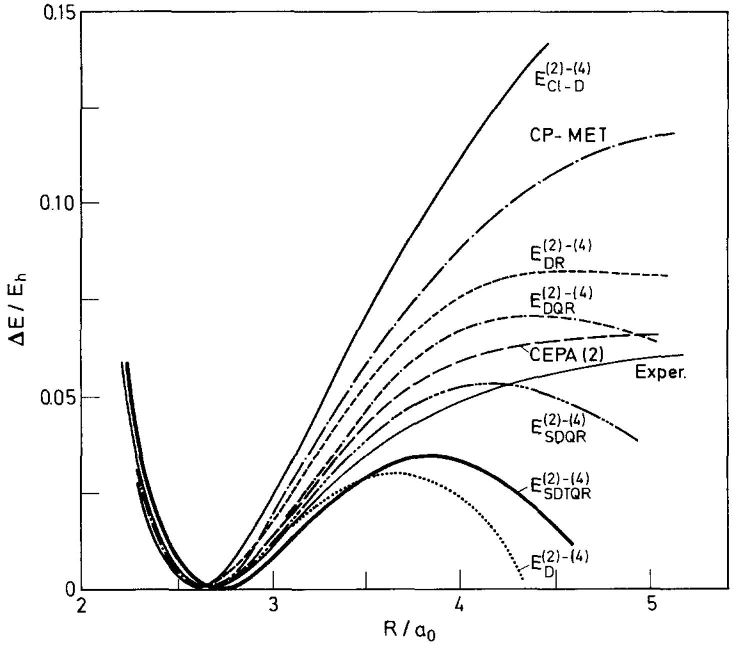

Fig. 1. Potential energy curves of F_2. [4s3p1d] basis. CP-MET and CEPA results are from Ref. [15].

4. Discussion

4.1. Spectroscopic Constants with [4s3p1d] Basis Set

From results presented in Table 3 it is evident that correlation effects improve SCF spectroscopic constants considerably, irrespective of the approximation used. Even the very simple second order result is quite satisfactory. However,

Table 2. SCF energy (in E/E_h) and valence-shell correlation contributions (in 10^3 E/E_h) of F_2 at various internuclear distances (in R/a_0). [5s4p2d1f] basis

R	$-E_{SCF}$	$-E^{(2)-(4)}_{STDQR}$	$-E^{(2)}_{D}$	$E^{(3)}_{D}$	$-E^{(4)}_{D}$	$-E^{(4)}_{S}$	$-E^{(4)}_{T}$	$-E^{(4)}_{Q}$	$E^{(4)}_{R}$	$-E^{(2)}_{D}S$
2.20	198.7291687	528.19	507.69	−2.07	7.37	3.50	14.70	7.12	14.27	42.99
2.30	198.7525552	534.58	513.41	−1.00	8.24	4.03	15.73	7.72	15.56	45.79
2.40	198.7647759	541.29	519.35	0.10	9.23	4.63	16.83	8.41	17.06	48.82
2.50	198.7687786	548.28	525.42	1.18	10.35	5.28	18.00	9.11	18.72	52.25
2.60	198.7667726	555.50	531.59	2.20	11.61	5.99	19.24	9.82	20.53	55.91
2.66	198.7633970	559.95	535.31	2.77	12.43	6.43	20.00	10.24	21.70	58.25
2.68	198.7619773	561.45	536.55	2.95	12.72	6.59	20.27	10.38	22.10	59.06
2.70	198.7604267	562.97	537.80	3.13	13.01	6.74	20.53	10.52	22.51	59.88
2.80	198.7510086	570.67	544.07	3.95	14.57	7.55	21.90	11.20	24.67	64.17
2.90	198.7394834	578.63	550.39	4.64	16.30	8.41	23.32	11.88	27.04	68.81
3.00	198.7265842	586.87	556.78	5.19	18.22	9.31	24.83	12.55	29.64	73.85
3.50	198.6566863	632.99	590.34	5.66	31.27	14.61	33.76	15.86	47.19	106.46
4.00	198.5954787	688.15	627.91	1.96	51.81	21.33	45.85	19.23	76.03	156.55
4.50	198.5487443	750.51	670.53	−6.19	81.99	29.37	62.01	22.84	122.41	232.29
5.00	198.5142471	814.28	718.21	−18.70	123.36	38.49	82.87	26.69	194.04	343.09

Table 3. Equilibrium distance (R_e), harmonic vibration frequency (ω_e), anharmonicity ($\omega_e x_e$) and vibration-rotation interaction constant (α_e) for F_2 in different approximations. [4s3p1d] basis

Energy	R_e, 10^{-10} m	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	α_e, cm^{-1}
SCF	1.331	1266	7.4	0.008
$E_{\text{D}}^{(2)}$	1.408	983	9.9	0.011
$E_{\text{D}}^{(2)-(3)}$	1.395	1011	10.5	0.011
$E_{\text{D}}^{(2)-(4)}$	1.417	909	14.5	0.014
$E_{\text{CI-D}}^{(2)-(4)}$	1.371	1115	8.6	0.010
$E_{\text{DR}}^{(2)-(4)}$	1.390	1032	10.2	0.011
$E_{\text{DQR}}^{(2)-(4)}$	1.399	999	10.7	0.011
CEPA(2)[a]	1.411	959	13.0	—
CP-MET[a]	1.394	1041	9.5	—
$E_{\text{SDQR}}^{(2)-(4)}$	1.410	952	11.8	0.012
$E_{\text{SDTQR}}^{(2)-(4)}$	1.429	877	14.1	0.014
Exper.[b]	1.412	917	11.2	0.014

[a] Ref. [15].
[b] Ref. [38].

going from the simplest second order up to the complete fourth-order, we cannot observe any straightforward gradual improvement, although clear trends may be easily seen within some subgroups of approaches. This is valid in the sequence $E_{\text{D}}^{(2)-(4)}$ (with no renormalization term and no quadruple-excitations), $E_{\text{DQR}}^{(2)-(4)}$ (with $E_{\text{R}}^{(4)}$ partly compensated by $E_{\text{Q}}^{(4)}$), $E_{\text{DR}}^{(2)-(4)}$ (with $E_{\text{R}}^{(4)}$ but no $E_{\text{Q}}^{(4)}$) and finally, $E_{\text{CI-D}}^{(2)-(4)}$ (which contains no $E_{\text{Q}}^{(4)}$ and at the same time the renormalization term is overestimated by disjoint $[-E_{\text{D}}^{(2)}S]_{\text{DJ}}$ terms). We see that spectroscopic constants obtained from CEPA (2) (and other variants of CEPA, see Ref. [15]) and CP-MET [15] also lie within the $E_{\text{D}}^{(2)-(4)}$ and $E_{\text{CI-D}}^{(2)-(4)}$ values. This limiting property of $E_{\text{D}}^{(2)-(4)}$ and $E_{\text{CI-D}}^{(2)-(4)}$ was observed previously for correlation energies of series of molecules in equilibrium geometry and it was more thoroughly discussed elsewhere [19, 20].

Further, it is worthwhile mentioning the very good agreement between CP-MET and $E_{\text{DQR}}^{(2)-(4)}$ (which is a fourth order approximation to CP-MET) spectroscopic constants. The agreement between CP-MET and $E_{\text{DQR}}^{(2)-(4)}$ was also described previously for correlation energies of series of molecules [17, 22], provided that MB-RSPT converged satisfactorily. Evidently, the bad convergence of MB-RSPT for larger distances (vide infra) does not deteriorate the basic interrelations of these two methods in calculations of spectroscopic constants.

Up to now we have been discussing methods which may be analysed in terms of double-excitation T_2 and quadruple-excitation T_2T_2 clusters, speaking in the language of CP-MET [39, 40]. If the T_1 and T_3 clusters, i.e. single and triple-excitations, are taken into account in the fourth-order MB-RSPT, we can recover another series $E_{\text{DQR}}^{(2)-(4)}$, $E_{\text{SDQR}}^{(2)-(4)}$ and $E_{\text{SDTQR}}^{(2)-(4)}$ with clear trends of all spectroscopic constants. Single-excitations improve $E_{\text{DQR}}^{(2)-(4)}$ spectroscopic constants considerably (their importance was mentioned also by Koch and Kutzelnigg [15]), but triples produce a too large correction. Consequently, the agreement with experiment is not so good as with singles alone. We may observe a larger influence from triple-excitations than from single-excitations, again in accord with results obtained for correlation energies of molecules in equilibrium geometry [7].

4.2. Potential Energy Curves with [4s3p1d] Basis Set

In analogy to the discussion of spectroscopic constants, one can start the discussion of potential energy curves by dividing various approximations into distinct subgroups. We can see that the sharing property of $E^{(2)-(4)}_{\mathrm{CI\text{-}D}}$ and $E^{(2)-(4)}_{\mathrm{D}}$ is valid over the whole range of investigated distances. Also trends after inclusion of $E^{(4)}_{\mathrm{R}}$ in the first step and $E^{(4)}_{\mathrm{Q}}$ in the second step are clearly indicated. We notice that in the improvement of the very bad behaviour of $E^{(2)-(4)}_{\mathrm{D}}$ (the maximum occurs at about $3.6\,a_0$) the crucial role belongs to the $E^{(4)}_{\mathrm{R}}$ contribution. In this sense we may also interpret the behaviour of the $E^{(2)-(4)}_{\mathrm{CI\text{-}D}}$ curve as the result of an overestimation of the (positive) renormalization term, due to the presence of the $[-E^{(2)}_{\mathrm{D}}S]_{\mathrm{DJ}}$ contribution.

Another group of results is formed by the sequence $E^{(2)-(4)}_{\mathrm{DR}}$, $E^{(2)-(4)}_{\mathrm{DQR}}$, $E^{(2)-(4)}_{\mathrm{SQDR}}$ and $E^{(2)-(4)}_{\mathrm{SDTQR}}$. From this series we see that quadruple, single and triple-excitations, all being negative, gradually deteriorate the qualitatively correct behaviour of the $E^{(2)-(4)}_{\mathrm{DR}}$ curve at larger distances (in the sense that they lead to a distinct maximum); without $E^{(4)}_{\mathrm{Q}}$, of course, $E^{(2)-(4)}_{\mathrm{DR}}$ underestimates the correlation energy, so that the curve goes too high over the experimental one. On the whole, the best seems to be CEPA(2), probably as the result of a very successful cancelation of the errors inherent to it: single determinant starting wave function, approximate investigation of bilinear terms in CP-MET, from which all CEPA variants may be inferred [15, 23, 24], neglection of triple (and single) excitations and finally the effect of the basis set. Other CEPA variants are not so successful in calculating the potential curve of F_2 [15]. In the light of our results, it does not seem correct to state that the best agreement of CEPA(2) with experiment is the result of the simulation of triple-excitations (this claim arises from the fact that in CEPA(2) the shift of energy in simplified CP-MET equations [15, 23, 24], which is the analogue to the fourth-order renormalization term in MB-RSPT, is underestimated). Also use of localized orbitals instead of canonical ones improves the results of CEPA(2) [15] (let us recall that CEPA(2) is not invariant with respect to unitary transformation among degenerate orbitals).

Up to now all our discussion of various fourth-order approximations in calculation of potential energy curves might be conducted in a similar lines as for spectroscopic constants and for correlation energies of molecules at equilibrium geometry. One important exception should be noted at this place, namely the very different potential energy curves obtained with CP-MET and $E^{(2)-(4)}_{\mathrm{DQR}}$. While at equilibrium distance both methods lead to very similar correlation energies, the problem of quasi-degeneracy between equilibrium ground state configuration and the $3\sigma_{\mathrm{g}}^2 \rightarrow 3\sigma_{\mathrm{u}}^2$ configuration at large interatomic distances is the reason of their different behaviour in this region. Also the great difference between $E^{(2)-(4)}_{\mathrm{DQR}}$

and $E_D^{(2)-(4)}$ and the incorrect behaviour of $E_D^{(2)-(4)}$ curve reflect the problem with quasi-degeneracy [41]. The fact that $E_D^{(2)-(4)}$ does not converge at large distances is well known. Taking double excitations to very high orders, the convergency may be compared for three interatomic distances (equilibrium, intermediate and large) in Table 5. The breakdown of $E_D^{(2)-(k)}$, as a result of its divergency at large distances, where quasi-degeneracy occur, is equivalent to the breakdown of the linear CP-MET (L-CP-MET), which becomes singular in this case. The careful analysis of the singularity of L-CP-MET and some model calculations were given by Paldus and co-workers [41–43]. Taking into account the non-linear terms in CP-MET [41–43] (or equivalently energy shifts in non-linear CP-MET equations [15]) improves the situation, although in cases of real degeneracy also single determinant CP-MET breaks down [42]. Methods to account for quasi-degeneracy within approximate CP-MET were suggested by Paldus et al. [42, 43].

In MB-RSPT the analogy to the "shift of energy" by the non-linear terms in CP-MET or CEPA methods is represented by renormalization term $E_R^{(4)}$ (i.e. by the fourth-order "EPV" terms, in the usual terminology), which is the only positive fourth-order term. Although it is partly compensated by $E_Q^{(4)}$, it still remains relatively effective in improving bad behaviour of double excitations at large distances. It is also interesting to note that the negative energy of the "net" effect of quadruple excitations, $E_Q^{(4)}$, rises with distance quite slowly. Consequently, at large distances $E_{QR}^{(4)}$, the total invariant contribution from fourth-order connected quadruple-excitation diagrams, remains highly positive. Although through these diagrams we investigated to some extent the $3\sigma_g^2 \rightarrow 3\sigma_u^2$ configuration, starting from single determinant RHF wave function we cannot expect a balanced description of correlation effects from all important configurations in situations where they become near-degenerate.

Other fourth-order contributions, $E_S^{(4)}$ and $E_T^{(4)}$ which are negative, rise with distance considerably (see Table 1) and thus lead to a pronounced maximum in the potential energy curve. They may be compensated only by higher-order renormalization terms, which may be positive [44, 45]. The importance of these terms in improving the potential energy curves may not be estimated seriously at present.

Starting from the single determinant RHF wave function, the only method which may be successful also in situations where the quasi-degeneracy occurs is probably the extended CP-MET, at least at the CCSD (Coupled Cluster Singles and Doubles) level [46]. In bond breaking processes it introduces higher order T_1T_2 clusters which may be important at large interatomic distances [46].

4.3. Results with Extended Basis Set

The situation where the improvement of the method (i.e. the inclusion of triple excitations in our case) deteriorates the agreement with experiment clearly demands the examination of the basis set. This is not so much important for the shape of the potential energy curve at larger distances, because here the situation

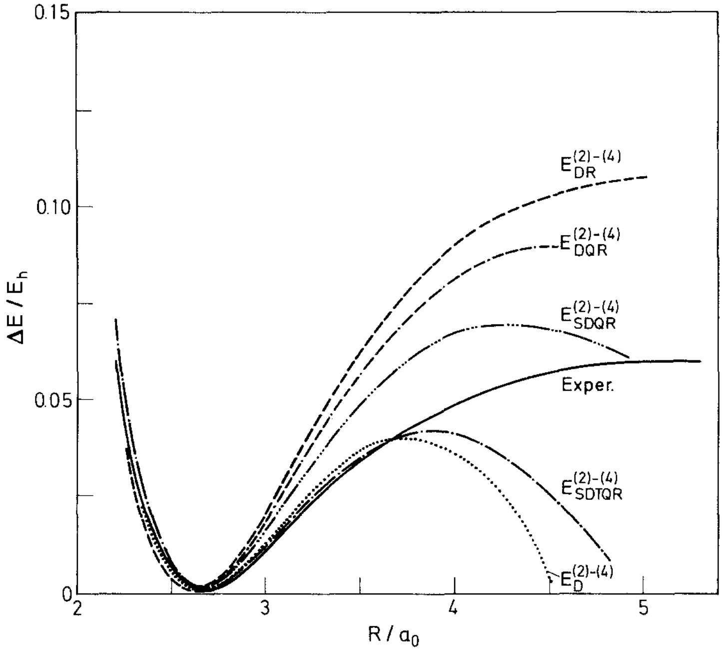

Fig. 2. Potential energy curves of F_2. [5s4p2d1f] basis

is rather clear. Namely, we cannot expect any substantial improvement of principal problems with quasi-degeneracy using extended basis, if we retain the single determinant starting wave function. In connection with potential energy curves it is sufficient just to mention that the $E_{SDTQR}^{(2)-(4)}$ curve (see Fig. 2) lies very close to the experimental one up to distances of about 3.7 a_0, i.e. up to 1.4 times the equilibrium distance. This should be quite sufficient in calculations of transition states. All trends in various approximations to the full fourth order discussed in the preceding section are valid also in the present case.

Much more interesting are calculations of spectroscopic constants, where the question, whether the single determinant fourth-order MB-RSPT is capable to provide values compatible with experiment is a principal question to be answered in this section. A look at results presented in Table 4 gives us the answer, that the agreement of $E_{SDTQR}^{(2)-(4)}$ values with experiment is really very good. The small error for the equilibrium distance, 0.008×10^{-10} m, we first tried to attribute partly to correlation effects from inner shells. Therefore we performed calculations for five distances around the equilibrium, including inner shell correlation energy. These results are presented in Table 6. Notice that, with these calculations we obtained about 86% of the "experimental" correlation energy at equilibrium distance (-0.725 E_h, see Ref. [47]), which is probably the largest value obtained so far. The effect of inner shells on R_e is quite small, however. We fitted five points from Table 6 and five points for the same distances with valence shell correlation only and obtained the decrease of R_e by 0.001×10^{-10} m after inclusion of inner shell correlation. ω_e and other spectroscopic constants remained unaffected.

Some contribution to the error in the calculated R_e may be expected also from the neglection of the relativistic effects. We estimated further a decrease of R_e by about 0.003×10^{-10} m, investigating relativistic effects by formula for the contraction of the covalent radius proposed by Pyykkö and Desclaux [48]. The residual small error in R_e may be attributed to the neglection of higher order contributions in MB-RSPT including neglection of correlation contributions from clusters not investigated in the fourth order (e.g. T_1T_2), to the effect which arises from using single determinant starting wave function and perhaps also to very small basis set effect.

From the Table 4 we may observe also quite good agreement of our $E^{(2)-(4)}_{\mathrm{SDTQR}}$ spectroscopic constants with the MC-SCF-CI calculations of Blomberg and Siegbahn [16]. In order to diminish the possible differences which may arise from different evaluation of spectroscopic constants, we performed the calculation of R_e and ω_e from Blomberg and Siegbahn's energies for distances up to $4.0\,a_0$. The result is $R_e = 1.417 \times 10^{-10}$ m, which is identical with the original result, and $\omega_e = 912\ \mathrm{cm}^{-1}$, which is higher by $2\ \mathrm{cm}^{-1}$. Bearing in mind the sensitivity of calculated ω_e to details in the fitting procedure [16], this result is quite satisfactory. We conclude, that both methods lead to almost identical results in the vicinity of equilibrium. The advantage of our $E^{(2)-(4)}_{\mathrm{SDTQR}}$ lies in its size extensivity, in contrast to MC-SCF-CI restricted to single and double excitations. Further, it is conceptually simpler and probably faster in comparison to MC-SCF-CI and at the same time it recovers more correlation energy. Of course, for larger distances, where our single determinant $E^{(2)-(4)}_{\mathrm{SDTQR}}$ breaks down, the MC-SCF-CI method is strictly preferred. Alternatively, the MB-RSPT must start from the multiconfiguration reference function. This, however, is a very difficult problem (see review [1]).

Table 4. Equilibrium distance (R_e), harmonic vibration frequency (ω_e), anharmonicity ($\omega_e x_e$) and vibration-rotation interaction constant (α_e) for F_2 in different approximations. [5s4p2d1f] basis

Energy	R_e, 10^{-10} m	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	α_e, cm^{-1}
SCF	1.329	1265	6.47	0.008
$E^{(2)}_{\mathrm{D}}$	1.400	1007	8.63	0.010
$E^{(2)-(3)}_{\mathrm{D}}$	1.386	1039	9.16	0.010
$E^{(2)-(4)}_{\mathrm{D}}$	1.407	946	12.1	0.012
$E^{(2)-(4)}_{\mathrm{DR}}$	1.379	1068	8.49	0.010
$E^{(2)-(4)}_{\mathrm{DQR}}$	1.388	1037	8.91	0.010
$E^{(2)-(4)}_{\mathrm{SDQR}}$	1.399	993	9.74	0.011
$E^{(2)-(4)}_{\mathrm{SDTQR}}$	1.420	913	11.7	0.013
MC-SCF-CI[a]	1.417	910	10.1	
Exper.[b]	1.412	917	11.2	0.014

[a] Ref. [16].

[b] Ref. [38].

Table 5. Convergency of double-excitations (energies in E/E_h) [4s3p1d] basis

Order of MB-RSPT	R/r_0		
	2.68	4.00	5.00
2	−0.43785	−0.53184	−0.62769
3	0.00435	0.00087	−0.02399
4	−0.01120	−0.04996	−0.12484
5	−0.00208	−0.02459	−0.08914
6	−0.00155	−0.02489	−0.10342
7	−0.00077	−0.02032	−0.10310
8	−0.00047	−0.01790	−0.10818
9	−0.00028	−0.01548	−0.11185
10	−0.00017	−0.01350	−0.11628
11	−0.00011	−0.01176	−0.12073
12	−0.00007	−0.01026	−0.12544

Finally, we would like to add two additional comments to the results, presented in Tables 3, 4 and 6. First, it is interesting to note that the main effect from the enlargement of the basis set on the spectroscopic constants is accounted for already with double excitations. The effect of triples (the most difficult case from the computational point of view) but also of singles and quadruples (expressed as $E^{(4)}_{\mathrm{QR}}$) is considerably constant in both the smaller and extended bases. This suggests the possibility of estimation of the difficult terms using the results with the smaller basis set. Alternatively, the scaling procedure introduced by Wilson [49] may be applied. This possibility deserves further examination. Second, there is also the possibility of investigating the effect of inner shell correlation at a simpler level. We can see from Table 6, that the inner shell correlation contribution is almost entirely included already in the second order. For example, for $R = 2.68\,a_0$ the total $E^{(2)-(4)}_{\mathrm{SDTQR}}$ energy leads to the effect of inner shells of $0.066\,02\,E_h$, whilst $E^{(2)}_{\mathrm{D}}$ to $0.064\,80\,E_h$.

5. Conclusions

The single determinant fourth-order MB-RSPT is a convenient method for calculations of the potential energy curve of F_2 around the equilibrium geometry. For larger distances it is reliable up to about $1.4\,R_e$. If this is valid for a wider class of systems, such reliability should be quite sufficient for calculations of the geometry and energy of transition states.

Full fourth order calculations with an extended basis set provide spectroscopic constants in very good agreement with experiment. R_e and ω_e for F_2 have a relative error of about 0.5% in comparison to experimental values. Although the accuracy of about 0.008×10^{-10} m for R_e and the accuracy of 4 cm^{-1} for ω_e is not excellent in comparison with the most precise experimental measurements,

Table 6. Correlation energy of F_2 (in 10^3 E/E_h) including inner shell. [5s4p2d1f] basis

R	$-E^{(2)-(4)}_{\mathrm{SDTQR}}$	$-E^{(2)}_{\mathrm{D}}$	$E^{(3)}_{\mathrm{D}}$	$-E^{(4)}_{\mathrm{D}}$	$-E^{(4)}_{\mathrm{S}}$	$-\mathrm{E}^{(4)}_{\mathrm{T}}$	$-E^{(4)}_{\mathrm{Q}}$	$E^{(4)}_{\mathrm{R}}$	$-E^{(2)}_{\mathrm{D}}S$	$-E^{(2)-(4)\,\mathrm{a}}_{\mathrm{IS}}$
2.60	621.58	596.45	1.29	11.72	6.13	19.86	9.86	21.15	63.29	66.07
2.66	625.99	600.12	1.86	12.54	6.59	20.65	10.28	22.34	65.86	66.03
2.68	627.48	601.35	2.04	12.83	6.75	20.92	10.42	22.75	66.75	66.02
2.70	628.98	602.59	2.22	13.12	6.90	21.19	10.56	23.16	67.65	66.01
2.80	636.64	608.79	3.04	14.68	7.72	22.59	11.24	25.36	72.36	65.97

[a] The difference of $E^{(2)-(4)}_{\mathrm{SDTQR}}$ (inner + valence) and $E^{(2)-(4)}_{\mathrm{SDTQR}}$ (valence).

the MB-RSPT may be very useful in prediction of spectroscopic constants for systems, not amenable to experiment.

Our investigations confirmed the results of MC-SCF-CI calculations [16], that even f-functions are necessary for obtaining an equilibrium bond distance in satisfactory agreement with experiment.

In applications of MB-RSPT to chemical reactivity one can hardly use the very extended basis set routinely. If we take as a typical smaller set a [4s3p1d] set, which is still relatively economic and at the same time it recovers all important correlation effects we recommend the use of an incomplete fourth-order MB-RSPT, preferably $E^{(2)-(4)}_{\mathrm{SDQR}}$. This approach is relatively tractable also for larger systems and, due to successful cancellation of deficiences in basis set and omitted contribution from triples, still quite accurate. This, of course, may not be valid for all systems (the dependence of the triple excitation components on the basis set and their relation to other fourth-order contributions has been discussed in the Ref. [50]).

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