# Fourth-order MB RSPT calculations of the reaction energy and the equilibrium constant of the reaction $1 / 2 \mathrm{~F}_{\mathbf{2}}+\mathbf{1 / 2} \mathrm{H}_{\mathbf{2}}=\mathbf{H F}$ 

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#### Abstract

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 $\mathrm{F}_{2}$, $\mathrm{H}_{2}$, and HF. Reaction heats and equilibrium constants of the gaseous phase reaction $1 / 2 \mathrm{~F}_{2}+1 / 2 \mathrm{H}_{2}=\mathrm{HF}$ 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 $\mathrm{F}_{2}, \mathrm{H}_{2}$ и HF. Теплоты реакций и константы равновесий реакции в газовой фазе $1 / 2 \mathrm{~F}_{2}+1 / 2 \mathrm{H}_{2}=\mathrm{HF}$ 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 $\mathrm{F}_{2}, \mathrm{H}_{2}, \mathrm{HF}$. 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 equilibriun 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 $\mathrm{F}_{2}, \mathrm{H}_{2}$, and HF was a Gaussian ( $9 s 5 p 1 d$ ) basis set contracted to $[4 s 3 p 1 d]$ with all six possible $d$ components included on fluorine [14] and ( $5 s 1 p$ ) set contracted to [ $3 s 1 p$ ] on hydrogen [15]. The hydrogen $s$-type functions were scaled by the factor 1.44. Exponents of the polarization functions were $\alpha_{\mathrm{d}}=1.4$ for fluorine [16] and $\alpha_{\mathrm{p}}=0.75$ for hydrogen.

For SCF calculations we used the POLYATOM/2 computer program [17] and SCF total energy converged at least to $10^{-8} E_{\mathrm{H}}$. 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 ( $R_{c}, B_{e}, \omega_{e}$, $\omega_{c} x_{e}, \alpha_{c}$ ), were calculated in the case of the $F_{2}$ curve from the first 10 energy values, in the case of the $\mathrm{H}_{2}$ 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 $\left(R-R_{c}\right) / R$ instead of $\left(R-R_{c}\right) / R_{c}$. The advantage of this modified procedure is its faster convergency. The total energy (i.e. $E_{\text {scr }}+$ 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 $E_{\mathrm{D}}^{(2)}, E_{\mathrm{D}}^{(3)}$, and $E_{\mathrm{D}}^{(4)} . E_{\mathrm{S}}^{(4)}$ is the fourth-order contribution

| $R / a_{0}$ | $E_{\text {SCr }} / E_{\text {H }}$ | $E_{\mathrm{D}}^{(2)} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(3)} / E_{\mathrm{H}}$ | $E_{\mathrm{S}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(4)} / E_{\mathrm{H}}$ | $E_{\bigcirc}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{R}}^{(4)} / E_{\mathrm{H}}$ | $E_{\text {SDor }}^{(4)} / E_{\text {H }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 $\mathrm{H}_{2}$

| $R / a_{0}$ | $E_{\mathrm{SCF}} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(2)} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(3)} / E_{\mathrm{H}}$ | $E_{\mathrm{S}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{S}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{R}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{SDOR}}^{(4)} / E_{\mathrm{H}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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 |


| $R / a_{0}$ | $E_{\text {SCF }} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(2)} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(3)} / E_{\mathrm{H}}$ | $E_{\mathrm{S}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{D}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{O}}^{(4)} / E_{\mathrm{H}}$ | $E_{\mathrm{R}}^{(4)} / E_{\mathrm{H}}$ | $E_{\text {SDOR }}^{(5)} / E_{\text {H }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 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. $E_{\mathrm{SDOR}}^{(4)}$ is a sum of the following terms: $E_{\mathrm{S}}^{(4)}, E_{\mathrm{D}}^{(4)}, E_{\mathrm{Q}}^{(4)}$, and $E_{\mathrm{R}}^{(4)}$. 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 $\mathrm{F}_{2}, \mathrm{H}_{2}$, 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: $E^{2}=E_{\mathrm{SCF}}+D_{\mathrm{D}}^{(2)}, E^{3}=E^{2}+E_{\mathrm{D}}^{(3)}, E^{4}=E^{3}+E_{\mathrm{SDOR}}^{(4)}$. $E_{\text {CI-SD }}^{(2)-(4)}$ is the fourth-order approximation to CI-SD, $E_{\text {Cl-SD }}^{(2)-(4)}=E_{\mathrm{D}}^{(2)}+E_{\mathrm{D}}^{(3)}+$ $+E_{\mathrm{D}}^{(4)}+E_{\mathrm{s}}^{(4)}+E_{\mathrm{R}}^{(4)}$.
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: $-0.11589,-0.07598,-0.06850,-0.06157,-0.05553 E_{\mathrm{H}}$.

Table 4

Spectroscopic constants of $F_{2}$

|  | $R_{\mathrm{c}} / 10 \mathrm{~m}^{-1}$ | $B_{\mathrm{c}} / \mathrm{cm}^{-1}$ | $\omega_{c} / \mathrm{cm}^{-1}$ | $\omega_{\mathrm{c}} x_{\mathrm{c}} / \mathrm{cm}^{-1}$ | $\alpha_{\mathrm{c}} / \mathrm{cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 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 |

Table 5
Spectroscopic constants of $\mathrm{H}_{2}$

|  | $R_{\mathrm{c}} / 10 \mathrm{~m}^{-1}$ | $B_{c} / \mathrm{cm}^{-1}$ | $\omega_{\mathrm{c}} / \mathrm{cm}^{-1}$ | $\omega_{c} x_{c} / \mathrm{cm}^{-1}$ | $\alpha_{\mathrm{c}} / \mathrm{cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 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 |

Table 6
Spectroscopic constants of HF

|  | $R_{\mathrm{c}} / 10 \mathrm{~m}^{-1}$ | $B_{\mathrm{c}} / \mathrm{cm}^{-1}$ | $\omega_{\mathrm{c}} / \mathrm{cm}^{-1}$ | $\omega_{c} x_{\mathrm{c}} / \mathrm{cm}^{-1}$ | $\alpha_{\mathrm{c}} / \mathrm{cm}^{-1}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 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 |

It is evident that in the case of the hydrogen molecule $E_{\mathrm{SDOR}}^{(4)}$ 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].
$\Delta E$ of the reaction considered, obtained from SCF energies of the investigated molecules calculated in experimental geometries led to the value $-304.4 \mathrm{~kJ} \mathrm{~mol}^{-1}$. For this reaction the estimated Hartree-Fock limit is $-299.8 \pm 4.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ [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 $\Delta H^{0}$ 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

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

Table 8. $\log K$ of the reaction $\frac{1}{2} \mathrm{~F}_{2}+\frac{1}{2} \mathrm{H}_{2}=\mathrm{HF}$

| T/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 |

results are very similar to SCF results. To our sorrow the most sophisticated approach $E^{4}$ led to $8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ error for $\Delta H_{0}^{0}$. 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 $\mathrm{F}_{2}$ and HF in experimental geometries the values -0.01367 and $-0.00444 E_{\mathrm{h}}$ [30]. This increases that error to $14 \mathrm{~kJ} \mathrm{~mol}^{-1}$. 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 $\mathrm{DZ}+\mathrm{P}$. 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 $\mathrm{NH}_{2}^{-}+$ $\mathrm{H}_{2}=\mathrm{NH}_{3}+\mathrm{H}^{-}$, 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 $\mathrm{DZ}+\mathrm{P}$ or better quality,
ii) using the RRHO approximation,
iii) calculation of $\omega_{e}$ by means of the second-order MB RSPT,
iv) calculation of $\Delta E$ using the best possible approach which includes correlation energy.

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