

**THE IMPACT OF HIGHER POLARIZATION FUNCTIONS
ON SECOND-ORDER DISPERSION ENERGY.
PARTIAL WAVE EXPANSION AND DAMPING PHENOMENON FOR He₂ ***

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Convergence properties of the Møller–Plesset dispersion energy with respect to saturation of polarization basis set have been investigated, by means of the partial wave expansion through “i” terms, for the He dimer. The expansion proved to be slowly convergent and ineffective if accurate calculations are aimed at. The damping functions for individual terms have been evaluated and shown to be in good agreement with the semi-empirical ones. The basis set extension effect, occurring when occupied and virtual orbitals of monomers are evaluated with the basis set of a whole dimer, has been found to improve upon the slow convergence of the partial wave expansion. Additional improvement is observed on adding bond-centered functions.

1. Introduction

The dispersion energy constitutes a very important, and in many cases dominant, attractive contribution to the interaction energies arising between atoms and molecules. Any potential, whether it is obtained ab initio or from the experiment, must account properly for the dispersion energy. One of the crucial problems of ab initio calculations of dispersion energies (in perturbation or supermolecular approach) is the basis set saturation. This problem was already addressed in the late sixties [1,2]. In particular, accurate representation of the dispersion effect requires higher polarization functions [3]. However, a relevant, detailed analysis has been reported only for the H–H interaction by Koide, Meath and Allnatt [4], who carried out accurate calculations of the partial wave expansion of the dispersion term. One of the conclusions has been that the partial wave approach, although very elegant and physically meaningful, is rather slowly convergent. More-

over, the studies on larger systems, Ne₂ [5,6] and very recently Ar₂ [7], showed that the higher terms in the partial wave expansion (i.e. also the higher polarization functions) are even more important for many-electron systems with p-type occupied orbitals than for H₂. There is no doubt now that the partial wave expansion, whether used by computational quantum chemists or semi-empirical potential builders, cannot be truncated at low-order terms. It is then of the utmost importance to get a much better insight into the properties of the partial wave expansion for systems other than H₂ and to make use of the acquired knowledge in the ab initio calculations as well as in model potentials studies. Ab initio calculations of damping functions are especially valuable for they provide the information about the damping phenomenon, the information which is independent of any experimental data. Ab initio damping functions allow us to design and check the damping functions of semi-empirical or semiquantitative nature.

At the same time one should analyze other approaches to calculations of dispersion energies. In particular, the Jezierski and van Hemert variational method with dimer centered basis set, cf.

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refs. [5,8–10], or the supermolecular approach, cf. refs. [11–13]. Although those methods lack the transparency of the partial wave expansion, or even, like supermolecular approach, do not separate dispersion from other contributions to the interaction energy, they take advantage of the enrichment of a monomer basis set by the partner's basis set [3,5,10].

This paper attempts to address the problems outlined above in the case of another important model system, the He dimer.

Section 2 begins with recalling briefly the definition and properties of the partial wave expansion for the dispersion energy. The variational method of Jeziorski and van Hemert [8] is also outlined and discussed. We restrict ourselves to the Møller–Plesset (MP) dispersion [8,14], i.e. we neglect completely the inter–intra-atomic electron correlation coupling. In section 3 the basis sets used throughout the calculations are described. The calculations of the dispersion energy by means of the partial wave expansion through R^{-16} are reported and analyzed in section 4. Section 5 provides the MP van der Waals coefficients and damping functions. Although the MP van der Waals coefficients are off by $\approx 25\%$ from the most accurate ones of Thakkar [15], the related damping functions are expected to be reliable for He₂ and agree well with the semiquantal ones of Tang and Toennies [16]. In section 6, the Jeziorski and van Hemert method with the dimer-centered basis set is applied to calculate the dispersion term. In particular, the basis set extension (BSE) effect, which occurs if the occupied and virtual orbitals are evaluated with the full dimer basis set, is investigated. In section 7 the effect of adding bond-centered functions to the basis set is analyzed. The results of adding bond-centered functions to the basis set is analyzed. The results of sections 6 and 7 are important also because they shed some light on the supermolecular calculations of the dispersion term which is then reproduced in the basis set of a whole complex. The BSE effect and bond-center functions are shown to be capable to improve the values of the dispersion term. Section 8 reports the most accurate up to date calculations of the MP dispersion energy in He₂.

2. Basic definitions

The dispersion energy between two spherically symmetric systems A and B may be written in the form of the partial wave expansion [4,5]

$$E_{\text{disp}}^{(2)} = \sum_{l_a, l_b=0} E(l_a, l_b), \quad (1)$$

where l_a and l_b stands for the angular quantum numbers of A and B, respectively. It is convenient to separate $E_{\text{disp}}^{(2)}$ into non-expanded long-range dispersion energies $E(n)$ (which have as their asymptotic limits the long-range multipolar dispersion energies varying as R^{-n}) and the short-range spherical dispersion contribution (vanishing as $\exp(-\alpha R)$) [4]:

$$E_{\text{disp}}^{(2)} = \sum_{n=6,8,10,\dots} E(n) + E_{\text{sph.disp}}, \quad (2)$$

where

$$E(n) = \sum_{l_a, l_b \geq 1}^{2(l_a + l_b + 1) = n} E(l_a, l_b). \quad (3)$$

$E(l_a, l_b)$ for $l_a, l_b \geq 1$ stands for the non-expanded dispersion energy related to the interaction of the instantaneous 2^{l_a} -pole of A and the instantaneous 2^{l_b} -pole of B. $E_{\text{sph.disp}}$ collects all $E(l_a, l_b)$ for which l_a and/or l_b equal zero. In the limit of large R we have

$$\lim_{R \rightarrow \infty} E(l_a, l_b) = -C(l_a, l_b)/R^{-2(l_a + l_b + 1)} \quad \text{for } l_a, l_b \geq 1, \quad (4)$$

$$\lim_{R \rightarrow \infty} E(l_a, l_b) = \mathcal{O}(e^{-\alpha R}) \quad \text{for } l_a \vee l_b = 0. \quad (5)$$

The total long-range coefficient C_n related to $E(n)$ is defined

$$C_n = \sum_{l_a, l_b \geq 1}^{2(l_a + l_b + 1) = n} C(l_a, l_b). \quad (6)$$

When constructing semi-empirical and empirical interatomic potentials it is convenient to separate the multipolar interaction from the charge overlap phenomenon and to introduce the notion of a “damping function” (see, e.g., refs. [17–19]). The damping function $f(l_a, l_b)$ may be defined as

a function which transforms the expanded partial wave component into the non-expanded one:

$$E(l_a, l_b) = -f(l_a, l_b)C(l_a, l_b)R^{-2(l_a+l_b+1)}. \quad (7)$$

$f(l_a, l_b)$ depends on R : $f(l_a, l_b) \rightarrow 0$ with $R \rightarrow 0$ and $f(l_a, l_b) \rightarrow 1$ with $R \rightarrow \infty$. It is often expedient to define a damping function f_n related to $E(n)$ rather than $E(l_a, l_b)$,

$$E(n) = -f_n C_n R^{-n}. \quad (8)$$

f_n may be easily expressed in terms of $f(l_a, l_b)$ and $C(l_a, l_b)$, $2(l_a + l_b + 1) = n$ (see eq. (12) of ref. [16]).

Eqs. (7) and (8) may be used to calculate damping functions in an ab initio manner. Ab initio calculations of $f(l_a, l_b)$ for simple model systems are very important since they may be used, after proper scaling, for other physically interesting interactions [16–23]. So far only for H₂ have highly accurate and complete calculations been performed [4]. For another important model system, the He dimer, an accurate evaluation of $E(l_a, l_b)$ would be extremely difficult because of the coupling between inter- and intra-atomic electron correlation.

However, one can still learn a lot if this coupling is neglected. In particular, such aspects as the convergence of the series (1) and the relation (7) should not be substantially affected by this coupling. Therefore, in this paper we report the calculations of the dispersion energy carried out with complete neglect of intra-atomic correlation effects. This dispersion energy, referred to as the “Møller–Plesset (MP) dispersion energy”, is for closed-shell systems defined by [8,24]

$$E_{\text{disp}}^{\text{MP}} = \sum_i^{\text{occ}} \sum_j^{\text{occ}} 4 \langle u_{ij} | v(12) | a_i b_j \rangle, \quad (9)$$

where a_i , b_j denote the orbitals of A, B, respectively, the summations are restricted to occupied orbitals, $v(12) = R^{-1} - r_{A2}^{-1} - r_{B1}^{-1} + r_{12}^{-1}$ (in au), and u_{ij} denotes the dispersion function [8,24]. To calculate u_{ij} , the variational procedure, described in detail in refs. [8,24], was employed. The ap-

proximate dispersion function takes then the form

$$u_{ij}(12) = \sum_{k \in A}^{\text{virt}} \sum_{l \in B}^{\text{virt}} (e_i^A + e_j^B - e_k^A - e_l^B)^{-1} \times \langle a_i b_j | v(12) | a_k b_l \rangle a_k(1) b_l(2), \quad (10)$$

where the basis sets $\{a_n\}$ and $\{b_m\}$ diagonalize the one-particle Fock operators h^A and h^B , respectively, providing the orbital energies e_n^A and e_m^B . Note that in general the symbols a and b do not indicate at which center the orbital is located. In the following two types of basis sets are considered.

(a) Monomer-centered basis set (MCBS) ^{*} $\{a_n\}$ ($\{b_m\}$) basis is obtained by diagonalizing h^A (h^B) operator within the space spanned by the atomic basis set of A (B) atom (cf. refs. [14,27]). Such an approach has been termed by Koide et al. [4] the “non-separable pseudo-state” approach. Although it is not necessary, it is convenient and elegant to carry out the calculations for each partial wave component of the dispersion energy separately.

(b) Dimer centered basis set (DCBS) $\{a_n\}$ ($\{b_n\}$) basis is obtained by diagonalizing h^A (h^B) operator within the basis set of the dimer (cf. refs. [5,8–10,28]). Strictly speaking, this is a “non-separable pseudo-state” approach too, the “states” are, however, calculated in the basis set which extends over the whole complex. Using the language of the valence bond theory, “ionic” and “exchange” structures are then allowed for in eq. (10) and the partial wave expansion is not useful any more. It should be stressed that the “exchange” structures have nothing to do with the exchange counterpart of the dispersion energy as defined in the symmetry-adapted perturbation theory. Their origin is not due to the imposing of the antisymmetry condition on the intersystem exchanges of electrons, but they make up for the incompleteness of the one-electron monomer-centered basis set. Due to the variational derivation of eq. (10) any extension of the basis set may only improve the result for $E_{\text{disp}}^{\text{MP}}$. The BSE effect to the space of the partner monomer, defined as

^{*} The terminology is that of Gutowski et al. [26].

the difference between the DCBS and MCBS calculations, must tend to zero with $l \rightarrow \infty$ (provided the set of orbitals at each l is also complete and one removes the linear dependences which can arise in DCBS). Those problems will be addressed in section 6.

To get some insight into the dependence of our results and conclusions on the MP approach, we also use the procedure of “shifting of denominators” as described by Kochanski [14]. Those results are referred to as “Epstein–Nesbet” (EN) results. In contrast to the MP approach, the EN approach gives for He₂ the values of C_n fairly close to the accurate, fully correlated values. The drawback of the EN approach is that the method is not bound and cannot be used to optimize the exponents of polarization basis functions [29]. The physical interpretation of the EN results may also be questioned (see, e.g., ref. [5]).

For the sake of convenience, in the following text we will often use letters to denote the l quantum number. For instance, $E(p, f)$ will stand for $E(1, 3)$. To distinguish between the MP and EN results we will use superscripts “MP” or “EN”, e.g., $E^{\text{MP}}(p, f)$.

To compute the dispersion energies the program of Groen and van Lenthe (INTACT) [25] was used.

3. Basis sets

Gaussian orbitals with spherical harmonics for angular parts [30] were employed. For the s symmetry we used the 15-term regularized even-tempered basis [31] as a primitive set.

The values of the exponents in the n -term set of the l symmetry ($l = p, d, \dots, i$) are given in table 1. For smaller sets the exponents were so chosen as to minimize the values of $E^{\text{MP}}(p, l)$ at $20.0 a_0^*$ (reoptimization at $5.6 a_0$ did not change the results significantly). Next, the exponents of larger basis sets were obtained by extrapolation. The

* It is of note that the exponents optimized for the dipole polarizability are very similar, only somewhat smaller than those in table 1 [32]. Optimization for higher polarizabilities has not been analyzed.

Table 1

The exponents of polarization gaussians for the He atom, used to calculate the dispersion energy in He₂

Basis set	Exponents (a_0^{-2})
1p	0.31821
2p	0.19427, 0.80311
3p ^{a)}	0.16979, 0.54175, 1.72852
3p ^{b)}	0.16686, 0.53965, 2.2786
4p ^{d)}	0.15, 0.4072, 1.1052, 3.0
5p ^{d)}	0.14, 0.3352, 0.8025, 1.9213, 4.6
1d ^{c)}	0.22896
2d ^{c)}	0.15293, 0.49871
3d ^{d)}	0.12, 0.3286, 0.90
4d ^{d)}	0.10, 0.2410, 0.5809, 1.4
5d ^{d)}	0.09, 0.1954, 0.4243, 0.9212, 2.0
1f ^{c)}	0.18360
2f ^{c)}	0.13594, 0.38407
3f ^{d)}	0.11, 0.2569, 0.60
4f ^{d)}	0.095, 0.2010, 0.4253, 0.90
5f ^{d)}	0.085, 0.1681, 0.3324, 0.6574, 1.3
1g ^{c)}	0.15840
2g ^{c)}	0.12032, 0.28393
3g ^{d)}	0.10, 0.2098, 0.44
4g ^{d)}	0.085, 0.1675, 0.3299, 0.65
5g ^{d)}	0.075, 0.1396, 0.2589, 0.4836, 0.9
1h ^{c)}	0.14558
2h ^{d)}	0.11, 0.225
1i ^{c)}	0.13934
2i ^{d)}	0.105, 0.200

^{a)} Optimal even-tempered basis set.

^{b)} From Chałasiński and Jeziorski [9].

^{c)} 2p set was used during optimization. ^{d)} Extrapolated.

extrapolation has been possible because of the distinct regularity one can observe when plotting, on a logarithmic scale, the exponents of the n -term l -symmetry basis set. In particular, for fixed n the lowest exponent and the distance between neighbor exponents for the same symmetry smoothly decrease with increasing l .

To compare the effectiveness of the l -symmetry sets of different sizes n , the values of $E^{\text{MP}}(p, l)$ were calculated at $5.6 a_0$ for $n = 1, 2$ and 3 , see table 2^{**}. As to the p sets, it is interesting to note that the optimal 3p even-tempered set is almost as efficient as the not even-tempered set from ref. [9]. Furthermore, the bulk of $E^{\text{MP}}(p, l)$

^{**} In this paper the energy units kelvin (K) and hartree (E_h) are used throughout. The conversion factor is: $1 E_h = 3.1578 \times 10^5 \text{ K}$.

Table 2

The values of $-E^{\text{MP}}(\text{p}, l)$, $l = \text{p}, \text{d}, \text{f}, \text{g}, \text{h}$ and i , at $5.6 a_0$. Energies in E_h

l	Number of polarization functions of l -symmetry		
	1	2	3
p ^{a)}	3.1724(−5)	3.5340(−5)	3.5634(−5) ^{b)} 3.5669(−5) ^{c)}
d ^{a,d)}	4.8345(−6)	5.0080(−6)	5.0154(−6)
f ^{a,d)}	1.1380(−6)	1.1779(−6)	1.1898(−6)
g ^{a,d)}	3.5435(−7)	3.8495(−7)	3.9359(−7)
h ^{c,e)}	1.3601(−7)	1.6555(−7)	–
i ^{c,e)}	5.7179(−8)	7.9772(−8)	–

^{a)} (10s) → [1s] from van Duijneveldt's tables [33].

^{b)} Optimal even-tempered 3p set.

^{c)} 3p set from Chałasiński and Jezierski [9] was used.

^{d)} 2p set from table 1 was used.

^{e)} (15s) → [1s] from Schmidt and Ruedenberg [31].

may be reproduced only with two exponents for the l -symmetry basis functions. However, when l increases the number of exponents for an l -symmetry set should be also increased to reproduce $E^{\text{MP}}(\text{p}, l)$ with a uniform accuracy. In fact, $E^{\text{MP}}(\text{p}, \text{h})$ and $E^{\text{MP}}(\text{p}, \text{i})$ are distinctly underestimated, if calculated with 1h and 1i basis sets,

respectively. This effect cannot be straightforwardly related to the underestimation of the corresponding $C^{\text{MP}}(\text{p}, l)$ coefficients. For instance, comparing the results obtained with the 1i and 2i basis sets we find that the values of $E^{\text{MP}}(\text{p}, \text{i})$ differ by 28.3% whereas the values of $C^{\text{MP}}(\text{p}, \text{i})$ differ only by 3.9%. The conclusion of practical value is that, whereas the long-range multipolar part of $E^{\text{MP}}(l_a, l_b)$ may be fairly well reproduced by even one-term basis sets, the reproducing of charge overlap effects may be much poorer (see also ref. [34]). Indeed, in the above discussed case the values of $f^{\text{MP}}(\text{p}, \text{i})$ differ by 25.4%.

4. Partial wave expansion of $E_{\text{disp}}^{\text{MP}}$

$E_{\text{disp}}^{\text{MP}}$ and its components were calculated in three physically different regions: strongly repulsive ($4.0 a_0$), van der Waals minimum ($5.6 a_0$) and weakly attractive ($7.0 a_0$). The values of $E^{\text{MP}}(n)$ and $E_{\text{sph,disp}}^{\text{MP}}$, along with their partial wave components, are presented in tables 3 and 4. Our best values for the total $E_{\text{disp}}^{\text{MP}}$, obtained with basis

Table 3

Individual partial wave components, $-E^{\text{MP}}(l_a, l_b)$ and $-E^{\text{MP}}(n)$, and the total $E_{\text{disp}}^{\text{MP}}$. The 1s3p2d2f2g2h2i basis was used. R in a_0 , energies in E_h

l_a-l_b	$-E^{\text{MP}}(n)$	$-E^{\text{MP}}(l_a, l_b)$			
		$R = 4.0$	$R = 5.6$	$R = 5.6^{\text{b)}$	$R = 7.0$
p–p	$-E(6) =$	2.3179(−4)	3.5669(−5)	3.5731(−5)	9.4772(−6)
2×(p–d)	$-E(8) =$	9.9636(−5)	1.0072(−5)	1.0188(−5)	1.8037(−6)
2×(p–f)		3.2927(−5)	2.38219(−6)	2.4539(−6)	3.0785(−7)
d–d		1.6280(−5)	1.1996(−6)	1.2531(−6)	1.5637(−7)
	$-E(10) =$	4.9207(−5)	3.5818(−6)	3.7070(−6)	4.6423(−7)
2×(p–g)		1.3412(−5)	7.8753(−7)	8.1990(−7)	7.8124(−8)
2×(d–f)		1.3631(−5)	7.9407(−7)	8.5238(−7)	8.0858(−8)
	$-E(12) =$	2.7042(−5)	1.5816(−6)	1.6723(−6)	1.5898(−7)
2×(p–h)		5.3497(−6)	3.3110(−7)		2.6288(−8)
2×(d–g)		5.7110(−6)	3.3439(−7)		2.7462(−8)
f–f		3.0437(−6)	1.6772(−7)		1.3967(−8)
	$-E(14) =$	1.4104(−5)	8.3321(−7)		6.7717(−8)
2×(p–i)		2.1190(−6)	1.5955(−7)		1.0831(−8)
2×(d–h)		2.0079(−6)	1.6353(−7)		1.1409(−8)
2×(f–g)		2.2588(−6)	1.6905(−7)		1.1733(−8)
	$-E(16) =$	6.3857(−6)	4.9213(−7)		3.3973(−8)
sum		4.2817(−4)	5.2230(−5)		1.2006(−5)
$-E_{\text{sph,disp}}$		1.8178(−5)	1.9040(−7)		2.0915(−9)
LARGE ^{a)}		4.7867(−4)	5.3789(−5)		1.2079(−5)

^{a)} Basis set described in section 8. ^{b)} Obtained with the 5p5d5f5g basis.

Table 4

Individual partial wave components $-E^{\text{MP}}(s_a, l_b)$ and the total spherical dispersion energy $-E_{\text{sph, disp}}^{\text{MP}}$. The 15s3p2d2f2g 1h1i basis was used. R in a_0 , energies in E_h

l_b	$-E^{\text{MP}}(s_a, l_b)(2 - \delta_{s_a l_b})$		
	$R = 4.0$	$R = 5.6$	$R = 7.0$
s	7.3058(-7)	6.3765(-9)	4.5816(-11)
p	5.7220(-6)	2.6458(-8)	1.1625(-10)
d	4.8728(-6)	3.7100(-8)	2.5640(-10)
f	3.2942(-6)	4.0745(-8)	4.3021(-10)
g	2.3301(-6)	3.5540(-8)	5.5370(-10)
h	8.7467(-7)	2.5179(-8)	3.5128(-10)
i	3.5310(-7)	1.9005(-8)	3.3780(-10)
sum	1.8178(-5)	1.9040(-7)	2.0915(-9)

LARGE (see section 8 for details), are also given in table 3.

One can see in table 3 and on fig. 1 that the convergence of the series of $E(n)$, $n = 2(l_a + l_b + 1)$, beginning with $E(10)$, is slow. At $5.6 a_0$ the ratio $E(n)/E(n+2)$, for $n = 6, 8, 10, 12$ and 14 , amounts to 3.5, 2.8, 2.3, 1.9 and 1.7, respectively, for the 3p2d2f2g2h basis. For the 5-term basis set the convergence is very similar. Such a pattern of

convergence resembles very closely the one observed in the H_2 [4] and Ne_2 [6] cases, as well as the " l^{-4} law" convergence observed for closed shell atoms [35]. Consequently, at $5.6 a_0$ the sum of $E(n)$ through $n = 12$ is still off by at least 5% from the accurate result. To get more accurate results one should first of all include higher $E(n)$. The sum of $E(n)$ through $n = 16$ is still off by 2% from the accurate result and $\approx 15\%$ of this discrepancy may be attributed to $E_{\text{sph, disp}}$. An accurate estimate of this small contribution is however hard to obtain. The partial wave expansion of $E_{\text{sph, disp}}$ is extremely slowly convergent hence even the first figure of our result may alter (see table 4). The same has been observed for H_2 [4]. In fact, the partial wave expansion is not very appropriate for calculations of $E_{\text{sph, disp}}$ as it is not for the spherical induction energy [36].

5. MP and EN calculations of van der Waals coefficients and damping factors

The values of C_n^{MP} and C_n^{EN} , for $n = 6(2)16$, and their $C(l_a, l_b)$ components are collected in

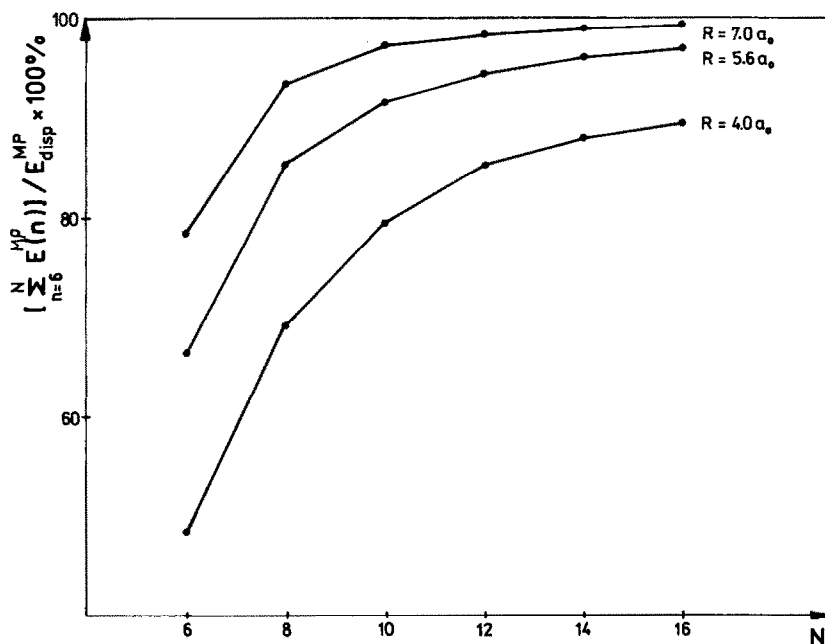


Fig. 1. The effectiveness of the truncated partial wave expansion in reproducing the total dispersion effect. The values of $\sum_{n=6}^N E^{\text{MP}}(n)/E_{\text{disp}}^{\text{MP}}$ are plotted versus N . The values of $E^{\text{MP}}(n)$ and $E_{\text{disp}}^{\text{MP}}$ (for LARGE basis) are taken from table 5.

table 5. They were obtained by calculating $E^{\text{MP}}(l_a, l_b)$ and $E^{\text{EN}}(l_a, l_b)$ at distances sufficiently large to make the overlap effects negligible. We expect that the values of C_n^{MP} for $n = 6(2)12$ are in error by less than 0.1% (the 5p5d5f5g basis) and for $n = 14, 16$ less than 5% (the 3p2d2f2g2h2i basis). As the EN approach is not bound we could observe a decrease of $|E^{\text{EN}}(l_a, l_b)|$ and $C_n^{\text{EN}}(l_a, l_b)$ with the improvement of the basis set (see also ref. [29]). In table 5 the accurate values of $C(l_a, l_b)$ calculated by Thakkar [15] are also given. It is interesting to note that C_n^{MP} are uniformly smaller, by $\approx 25\%$, than the related accurate C_n . Such regularity is not observed for C_n^{EN} . This should be considered as another undesirable feature of the EN results.

The values of damping functions f_n^{MP} and f_n^{EN} are given in table 6 while those of $f_n^{\text{MP}}(l_a, l_b)$ are in table 7. They were calculated for a few distances which for a given n cover the region of the fastest growth of the damping effect. The distance $5.6 a_0$, which is close to R_c has also been considered. The same basis sets as in the calculations of C_n were used, i.e. the 1s3p2d2f2g2h1s basis. It is important to note that according to Bukta and Meath [34] (see also section 3) the damping func-

tions are substantially more sensitive to the choice of a basis set than the C_n coefficients. We expect that the values of $f_n^{\text{MP(EN)}}$ for $n = 6(2)12$ are in error by less than 5% (the 5p5d5f5g basis). For $n = 14, 16$ (the 3p2d2f2g2h2i basis) the error can reach 20% in the region of strong damping and 10% in the region of weak damping.

One can notice that the values of f_n^{EN} are very close to the values of f_n^{MP} (the difference seldom exceeds 3%), and the former are systematically slightly lower. These results allow us to expect that the MP damping functions are not substantially altered by the apparent intra-atomic correlation effects. (Note, however, that the EN method may be reduced to the shift of denominators in the MP expression for the dispersion energy and accounts for only a part of apparent intra-atomic correlation [5].) Similarly, according to Krauss et al. [38] the true intra-atomic correlation effects do not significantly affect $f(p, p)$ either. The above results let us expect that in practice the MP damping functions could be applied to damp accurate coefficients C_n .

Our calculations of f_n^{MP} and f_n^{EN} confirm the important feature of damping functions that individual $C_n R^{-n}$ components should be damped sep-

Table 5

The values of the van der Waals coefficients $C^x(l_a, l_b)$ and C_n^x , $x = \text{MP, EN}$. C_n in $a_0^n E_h$

n	$l_a - l_b$	MP ^{d)}	MP ^{e)}	EN ^{d)}	EN ^{e)}	Literature values
6	p-p	1.118	1.116	1.454	1.488	$C_6^{\text{MP}} = 1.10$ ^{a)} , 1.12 ^{b)} ; $C_6 = 1.46$ ^{c)}
8	2×(p-d)	10.527	10.483	13.202	13.541	$C_8^{\text{MP}} = 12.8$ ^{a)} ; 10.52 ^{b)} ; $C_8 = 14.11$ ^{c)}
10	2×(p-f)	90.574	90.281	111.050	113.380	$2 \times C(p, f) = 119.50$ ^{c)}
	d-d	46.352	46.031	56.301	57.831	$C(d, d) = 64.09$ ^{c)}
	$C_{10}^{\text{MP}} =$	136.926	136.312	$C_{10}^{\text{EN}} =$	171.211	$C_{10} = 183.6$ ^{c)}
12	2×(p-g)	1214.95	1211.74	1466.04	1491.76	$2 \times C(p, g) = 1550 \pm 30$ ^{c)}
	2×(d-f)	1282.44	1274.87	1525.98	1560.98	$2 \times C(d, f) = 1751.2$ ^{c)}
	$C_{12}^{\text{MP}} =$	2497.39	2486.61	$C_{12}^{\text{EN}} =$	3052.74	$C_{12} = 3300 \pm 30$ ^{c)}
14	2×(p-h)		22985.3		27895.1	
	2×(d-g)		25103.8		30178.7	
	f-f		12948.8		15472.2	
	$C_{14}^{\text{MP}} =$		61037.9	$C_{14}^{\text{EN}} =$	73546.0	
16	2×(p-i)		572160.4		686756.6	
	2×(d-h)		656803.1		779289.3	
	2×(f-g)		703188.8		825643.4	
	$C_{16}^{\text{MP}} =$		1932152.3	$C_{16}^{\text{EN}} =$	2291689.2	

^{a)} Szalewicz and Jeziorski [37]. ^{b)} Chałasiński and Jeziorski [9]. ^{c)} Thakkar [15]. ^{d)} Obtained for the 5p5d5f5g basis.

^{e)} Obtained for the 3p2d2f2g2h2i basis.

Table 6

The values of damping functions f_n^x , $n = 6(2)16$, $x = \text{MP, EN}$ and TT (TT from ref. [16]). R in a_0

n	R	$f_n^{\text{MP a)}}$	$f_n^{\text{MP b)}}$	$f_n^{\text{EN c)}}$	f_n^{TT}
6	1.5	0.0802	0.0770	0.0758	0.0718
	2.5	0.4065	0.4059	0.3935	0.3889
	3.5	0.7560	0.7421	0.7456	0.7284
	4.5	0.9271	0.9213	0.9227	0.9103
	5.6	0.9859	0.9857	0.9848	0.9792
8	2.5	0.1577	0.1510	0.1518	0.1497
	3.5	0.4846	0.4705	0.4755	0.4573
	4.5	0.7782	0.7529	0.7724	0.7447
	5.5	0.9275	0.9193	0.9253	0.9062
	5.6	0.9360	0.9293	0.9340	0.9161
10	3.0	0.1178	0.1104	0.1138	0.1106
	4.0	0.3931	0.3785	0.3862	0.3611
	5.0	0.6918	0.6597	0.6866	0.6464
	5.6	0.8211	0.7970	0.8177	0.7790
	6.5	0.9321	0.9256	0.9306	0.9048
12	3.5	0.0911	0.0820	0.0884	0.0826
	4.5	0.3212	0.3093	0.3158	0.2839
	5.6	0.6369	0.6050	0.6324	0.5772
	6.0	0.7339	0.7038	0.7303	0.6730
	7.5	0.9409	0.9364	0.9400	0.9050
14	4.5		0.1443	0.1417	0.1281
	5.5		0.3813	0.3766	0.3386
	5.6		0.4072	0.4024	0.3634
	6.5		0.6391	0.6346	0.5868
	8.0		0.9074	0.9057	0.8555
16	5.0		0.1176	0.1160	0.0981
	5.6		0.2383	0.2353	0.1924
	6.5		0.4570	0.4532	0.3867
	8.0		0.8029	0.8006	0.7159
	9.0		0.9298	0.9290	0.8611

a) Obtained with the 5p5d5f5g basis.

b) Obtained with the 3p2d2f2g2h2i basis.

c) Obtained with the 5p5d5f5g basis set for $n = 6, 8, 10, 12$, and with the 3p2d2f2g2h2i basis for $n = 14, 16$.

arately (see refs. [4,16,19,21,23]). Interestingly, the values of the $f(l_a, l_b)$ related to the same n are very similar but not identical, even for the largest 5-term polarization sets (see table 7). The difference is usually larger in the region of strong damping (up to 4.3%). Moreover, the larger the difference $|l_a - l_b|$, the larger $f(l_a, l_b)$. According to Knowles and Meath [7] the discrepancy between the values of the $f(l_a, l_b)$ related to the same n , results only from the unsaturation of the basis set. For Li₂ the 4-term polarization sets were

Table 7

The basis set dependence of $f(l_a, l_b)$ contributing to f_{10} and f_{12} . R in a_0

R	$l_a - l_b$	Basis sets		
		3p2d2f2g	4d4p4f4g	5p5d5f5g
3.0	p-f	0.1116	0.1180	0.1188
	d-d	0.1080	0.1154	0.1158
4.0	p-f	0.3824	0.3916	0.3947
	d-d	0.3708	0.3853	0.3899
5.0	p-f	0.6638	0.6913	0.6930
	d-d	0.6516	0.6895	0.6896
6.5	p-f	0.9276	0.9298	0.9326
	d-d	0.9218	0.9279	0.9311
3.5	p-g	0.0824	0.0922	0.0932
	d-f	0.0817	0.0888	0.0892
4.5	p-g	0.3185	0.3224	0.3257
	d-f	0.3006	0.3123	0.3169
6.0	p-g	0.7156	0.7367	0.7387
	d-f	0.6925	0.7278	0.7294
7.5	p-g	0.9414	0.9417	0.9448
	d-f	0.9316	0.9342	0.9372

sufficient to suppress the above discrepancy [7]. Our calculations neither confirm nor falsify the Knowles and Meath hypothesis since in our case the values of the f_n did not reach the complete basis limit.

To compare our results with previous approximations of damping functions for He₂ we have supplemented fig. 3 published by Tang and Toennies [16] with the present results and those of Krauss et al. [38] (fig. 2). Among the damping functions presented on fig. 2 only those of Jacobi and Csanak [39], Krauss et al. [38] and ours have been obtained in a fully ab initio way. The present results agree well with Jacobi and Csanak, but, since they calculated only f_6 , the comparison cannot be comprehensive. The results of Krauss et al. are substantially smaller than ours, and the discrepancy increases with increasing n . However, Krauss and Neumann's results are expected to underestimate f_n (cf. the discussion in ref. [16]). When comparing our results with non-ab initio ones, in the region of strong damping, the best agreement is observed with recent Tang and Toen-

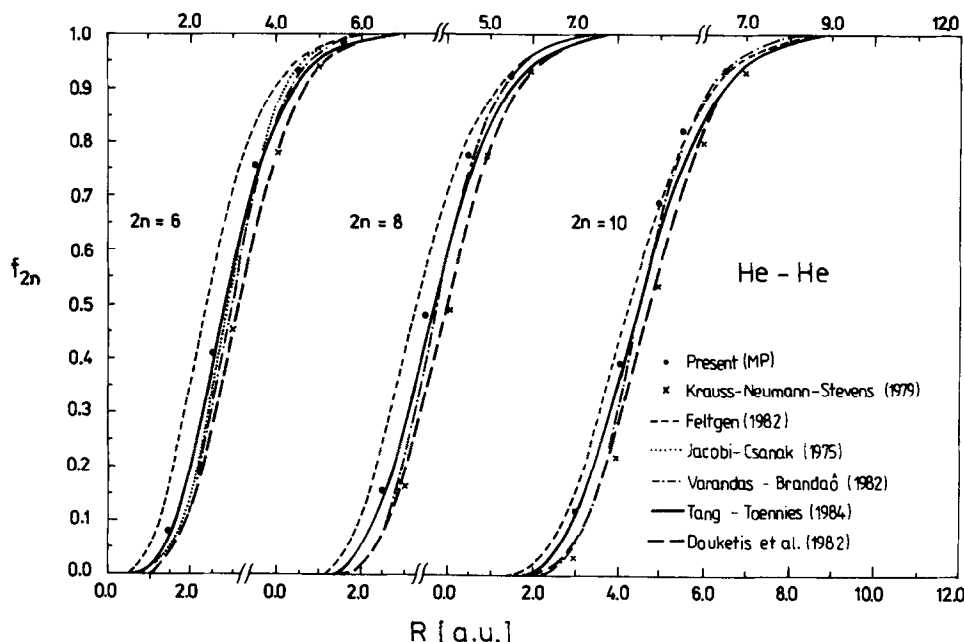


Fig. 2. Comparison of the present damping functions for $2n = 6, 8$ and 10 for He₂ with the model and ab initio damping functions from the literature.

nies damping functions [16], the latter being somewhat smaller than ours for $n = 6, 8, 10$. The difference between f_n^{MP} and f_n^{TT} increases with increasing n , however, and becomes more pronounced for $n \geq 12$. Some disagreement between non-ab initio and ab initio calculated damping functions is not surprising. On the one hand, semi-empirical or semiquantitative damping functions have to make up for some other or less obscure effects neglected by a particular model of interac-

tion. On the other hand, our results are not fully error-free: the inter-intra correlation coupling has been neglected and some unsaturation of the basis set, in particular for the largest l , also exists.

6. Basis set extension to the space of the partner

There are at least two important reasons for studying the (BSE) effect arising when one switches from MCBS to DCBS:

Table 8

The basis set extension effect to the space of the partner. The values of $-E_{\text{disp}}^{\text{MP}}$ calculated within the MCBS and DCBS approaches. The atom-centered basis sets were built from the 1s3p2d2f2g1h1i set. Energies in E_h , distances in a_0

Atoms centered basis up to	$R = 4.0$		$R = 5.6$	
	MCBS	DCBS	MCBS	DCBS
p	2.3179(-4)	2.7867(-4)	3.5669(-5)	3.7221(-5)
d	3.4771(-4)	4.1036(-4)	4.6941(-5)	4.8517(-5)
f	3.9731(-4)	4.4899(-4)	5.0285(-5)	5.1782(-5)
g	4.1904(-4)	4.5813(-4)	5.1621(-5)	5.2944(-5)
h	4.2207(-4)	4.5950(-4)	5.2057(-5)	5.3159(-5)
i	4.2306(-4)	4.6031(-4)	5.2241(-5)	5.3254(-5)
LARGE ^{a)}		4.7867(-4)		5.3789(-5)

^{a)} Basis set described in section 8.

(1) The partial wave expansion turned out to be rather slowly convergent. Improvement of the virtual space by including the basis set of the partner was recognized already by Certain and Hirschfelder [40] and studied later by Chałasiński et al. [3,5,10] (cf. also ref. [27]).

(2) Calculations of interaction energies by the supermolecular approach reproduce the dispersion term in the basis set of a whole dimer. Perturbation calculations of this effect, to be compatible, should be carried out with the same basis set [11].

To analyze the BSE effect as the function of the basis set saturation, $E_{\text{disp}}^{\text{MP}}$ was computed both within the MCBS and DCBS approaches using the sequence of the basis sets built of the 1s3p2d2f2g1h1i set. The resulting values of $E_{\text{disp}}^{\text{MP}}$, for $R = 4.0$ and $5.6 a_0$, are in table 8. At first sight one observes that the BSE improves considerably the values of $E_{\text{disp}}^{\text{MP}}$ and that in practice we are far from being threatened by the abovementioned overcompleteness. The profits from the BSE are pronounced for low l and small R . Therefore, one can say that the BSE can mimic the polarization functions which are missing in the related MCBS calculation. Indeed, the values of $E_{\text{disp}}^{\text{MP}}$ obtained within the DCBS approach and with the basis set up to l -symmetry functions are, starting with sufficiently high l , systematically better than $E_{\text{disp}}^{\text{MP}}$ obtained within the MCBS approach and with the basis set up to $(l+1)$ -symmetry functions. This is observed for 4.0, 5.6 and 7.0 a_0 beginning with $l = 2, 3$ and 4, respectively.

Another interesting feature of the BSE effect is that for high l the improvement of $E_{\text{disp}}^{\text{MP}}$ due to the l -symmetry functions can be much lower in the DCBS than in the MCBS approach. For example, at $R = 4.0 a_0$, the gain from the g symmetry is 6.86 K for the MCBS approach but only 2.86 K for the DCBS approach. Consequently one observes slow decreasing of the global BSE effect as l increases, in the region of high l .

7. Effectiveness of bond-centered basis functions in simulating higher polarization functions

The slow convergence of dispersion energies calculated both with MCBS and DCBS orbitals

motivated an examination of the usefulness of bond-centered basis functions. Enriching the basis set with the bond-centered orbitals is perfectly legitimate due to the variational character of eq. (10). Using bond-centered functions has been advocated by Burton [41] who, together with Senff, applied them in recent calculations for HeH₂ [42] and He₂ [43]. The original goal was to minimize BSSE (basis set superposition error) by proper choice of displacements and exponents. In this paper we are rather interested in using bond functions to simulate missing higher polarization functions of low exponents, necessary to calculate the dispersion energy.

In table 9 the values of $E_{\text{disp}}^{\text{MP}}$ are presented, calculated within the DCBS approach with the basis set of atom-centered gaussians augmented by two groups of bond functions equidistant from the nuclei. The set of bond functions consisted of one s gaussian ($\alpha = 0.65$) and three p gaussians ($\alpha = 0.40$). The values of the exponents have been the same as those used by Senff and Burton [43]. The displacement from the nucleus, denoted by ρ , was optimized for each R and was the same for s and p functions. Perusal of the results of table 9 leads to the following conclusion. The atom-centered basis sets, which contain up to l -symmetry functions, after adding bond functions yield

Table 9

Effectiveness of bond-centered functions. The atom-centered basis sets were built from the 1s3p2d2f2g set, the bond-centered functions were: 1s (0.65) and 1p (0.40), displayed by ρ from the atoms. All non-zero displacements were optimized. Energies in E_h , distances in a_0

Atom-centered basis up to	$R = 4.0$		$R = 5.6$	
	ρ	$-E_{\text{disp}}^{\text{MP}}$	ρ	$-E_{\text{disp}}^{\text{MP}}$
p	0	2.9467(−4)	0	3.7438(−5)
	1.25	4.2863(−4)	1.4	5.0724(−5)
d	0	4.2004(−4)	0	4.8796(−5)
	1.9	4.4908(−4)	2.0	5.2604(−5)
f	0	4.5428(−4)	0	5.1993(−5)
	0.95	4.6345(−4)	2.4	5.3154(−5)
g	0	4.6153(−4)		
	0.90	4.7191(−4)		

usually better results than pure atom-centered basis sets including up to $(l+1)$ -symmetry functions. This fact is of practical significance since reducing the highest value of l and adding bond functions instead will in general reduce the size of a basis set and will remove the most time-consuming integrals.

The usefulness of bond functions in the supermolecular calculations of interaction energies may be questioned for two reasons. First, the bond functions are supposed to generate large BSSE [44] which is commonly regarded as a warning that a basis set may not be appropriate for a particular problem. Secondly, to ensure the same accuracy of the dispersion component through the whole potential surface, a time-consuming reoptimization of displacements and exponents of bond functions seems to be unavoidable. To analyze the first objection the supermolecular calculations of the interaction energy were carried out for He_2 by the CEPA-1 method [45]. It has been found that the addition of bond functions leads to a significant lowering of the monomer energies and a substantial BSSE. However if the function counterpoise method [46] is applied the value of the interaction energy is in good agreement with the perturbation estimate of this quantity, for the same basis set [45].

As to the second objection, the numerical results are also optimistic. We have found that in a wide range of ρ $E_{\text{disp}}^{\text{MP}}$ is a slowly varying function of the displacement. For example, at $R = 5.6 a_0$ if the atom-centered part of the basis set includes up to p functions the values of $E_{\text{disp}}^{\text{MP}}$ are varying by less than 0.35 K for $\rho \in [0.8 a_0, 2.0 a_0]$, whereas the maximal gain from adding bond functions has been found to be 4.2 K. At $5.6 a_0$, for optimal displacements, we have also reoptimized the exponents of bond functions by uniform scaling. The improvement of $E_{\text{disp}}^{\text{MP}}$ turned out, however, to be less than 0.08, 0.02 and 0.01 K if the atom-centered part of the basis sets includes up to p, d and f functions, respectively. Clearly, adding bond functions is a profitable procedure. However, if the uniform accuracy of the dispersion term through the whole potential surface is to be achieved, a rough optimization of bond functions parameters is necessary for each point of the surface.

8. Accurate calculations of $E_{\text{disp}}^{\text{MP}}$

Finally, we tried to calculate $E_{\text{disp}}^{\text{MP}}$ with a largest feasible atom-centered basis set augmented by bond functions and employing the DCBS approach. This basis set is denoted as LARGE. It consists of the 10s3p2d2f2g1h1i set plus the bond functions described in section 7, displaced from the nuclei by 0.85, 2.6 and 3.3 a_0 for $R = 4.0, 5.6$ and 7.0 a_0 , respectively. The 10s set was built of the 15s set (see section 2), contracted as $[9 \times 1, 6]$. The values of $E_{\text{disp}}^{\text{MP}}$ are in table 3.

At 5.6 a_0 our result -16.99 K, may be compared to the best previous one, -16.90 K, obtained with explicitly correlated gaussians [37]. Our $E_{\text{disp}}^{\text{MP}}$ is then slightly better, but we expect that the exact value of $E_{\text{disp}}^{\text{MP}}$ may be still lower by even 0.1 K. One cannot help remarking what a hard task does computation of the interaction energy present for He_2 if one aims at the accuracy of 0.1 K. Such accuracy is necessary to match the semi-empirical and empirical predictions [47]. In our opinion, the excellent agreement of even the best ab initio calculations for He_2 [41,48,49] ^{*} with experimental data must result from more or less obscure balance of basis sets and methodological errors.

9. Conclusions

Not sufficiently fast convergence of the partial wave expansion of E_{disp} makes reliable evaluation of interaction energies particularly hard for complexes where the dispersion effect is a dominant contribution. A good illustration of this may be obtained by using a popular “SCF + $E_{\text{disp}}^{\text{MP}}$ ” approximation of the interaction energy and analyzing the effect of truncation of the dispersion energy at successive n in eq. (2). At $R = 5.6 a_0$, truncation at $n = 6, 8, 10$ and 12 causes the error of 73%, 32%, 17% and 10%, respectively, with respect to the interaction energy calculated with LARGE basis (the SCF interaction energy was taken from ref. [32]).

^{*} See also Lin and McLean as cited in refs. [50,51] and Meyer and Reinsch as cited in ref. [51].

Consequently, if the dispersion is calculated from the multipole expansion (as in model potentials) the expansion should be quite long. The effectiveness of a truncated partial wave expansion in reproducing the total dispersion contribution is demonstrated on fig. 1. Furthermore, individual terms in the multipole expansion must be damped separately [4,16,19,21,23]. Reliable ab initio damping functions for He₂, f_n^{MP} , have been reported in table 6.

If the dispersion term is reproduced ab initio (by perturbational method for supermolecular approach) even quite high polarization functions may be necessary to match the accuracy of contemporarily available experimental data. It should be strongly stressed that none of the existing ab initio calculations for He₂ [41,48,49] meets fully those requirements and their accuracy must be attributed to more or less obscure balance of basis set and methodological errors. Unfortunately, the situation becomes even worse if monomer occupied orbitals are of p-symmetry [6,7]. Although we have shown that the basis set extension effect (in the supermolecular approach it is implicitly accomplished) and bond functions improve the results, very large basis sets with higher- l functions seem to be unavoidable anyway.

On the basis of our numerical evidence we can give some guidelines how to extend systematically the set of polarization functions for calculations of $E_{\text{disp}}^{\text{MP}}$. Prescription for the polarization basis sets depends on the distance between the interacting atoms and on the approach, MCBS or DCBS. Obviously, due to the $R^{-2(l_a+l_b+1)}$ dependence, the role of high- l polarization functions decreases with increasing R . Let us focus then on the distance $R_e = 5.6 a_0$. One may order various polarization functions according to their ability to improve $E_{\text{disp}}^{\text{MP}}$ calculated within the MCBS approach. Denoting by $l^{(n)}$ the n -terms basis set of l -symmetry one gets the following arrangement:

$$p^{(1)} > d^{(1)} > p^{(2)} \gtrsim f^{(1)} > g^{(1)} > p^{(3)} \approx d^2 \approx h^{(1)}. \quad (11)$$

From the above arrangement the following string of basis sets results: 1p, 1p1d, 2p1d1f, 2p1d1f1g, 3p2d2f1g1h. For each member of this string the

error of $E_{\text{disp}}^{\text{MP}}$ is of the same order of magnitude per symmetry. Interestingly, our arrangement resembles very closely that of Ahlrichs et al. [52] (to see this one should increase all the l in (9) by one as the valence orbitals of the atoms studied in [52] are of p-symmetry). However, since the basis sets in [52] are designed for the correlation energy of chemically bonded atoms the values of exponents are larger than those optimal for the dispersion interaction between closed shell atoms. (See section 3 and refs. [3,6].)

It should be stressed that the arrangement (9) may serve as a guideline rather than as a strict prescription. Indeed, the gain from high- l functions is much higher in the MCBS approach than in the DCBS approach, see section 6. In the latter approach, for extended polarization sets, the monomer centered basis sets which are richer in low- l functions and poorer in high- l functions may be more effective. Indeed, for instance at $5.6 a_0$, $E_{\text{disp}}^{\text{MP}}$ is -16.15 K for the 5s2p1d1f1g basis set and -16.28 K for the 5s3p2d1f basis set.

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