AN ANALYSIS OF THE PARTIAL WAVE EXPANSION OF THE DISPERSION ENERGY FOR Ne_2 *

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Calculations of the dispersion energy for Ne_2 by using the partial wave expansion through the h–h term were carried out in the region of the van der Waals minimum. It is shown that, at $R \approx 6a_0$, lack of higher than d orbitals gives a dispersion energy in error by ≈16%, and lack of higher than f orbitals gives an error of ≈6%.

1. Introduction

Recently, in his review article on intermolecular interactions, Scoles concluded that "intermolecular forces have entered the age of spectroscopic precision" [1]. In particular, this is the case for the rare-gas dimers, where precise potentials reproducing accurately a variety of dilute-gas properties have recently been published (He_2 [2], Ne_2 [3], Ar_2 [4,5]). Consequently, more than ever before, in order that ab initio calculations be useful they should be of high quality and should give special attention to defining what has been left out of the calculations.

Ab initio calculations of the non-expanded dispersion contribution to the interaction energy rarely take into account higher than d polarization functions. To the best of our knowledge, f functions were used (except for small model systems, He_2 [6,7] and Be_2 [8]) only for the Ne dimer [9] and Ar–HCl [10], whereas higher than f functions have never been used.

In many cases, when a 10% or larger error in the interaction energy is acceptable, this limitation does not seem to be serious. In addition, since the interaction potential is the net result of a balance of repulsive and attractive contributions, quite often fortuitous cancellation of errors may occur and obscure the actual role of higher polarization functions. For instance, a simple ab initio approximation of the interaction energy as the sum of the SCF interaction energy and the dispersion contribution (SCF–DISP) [11,12] may work quite well for rare-gas dimers without higher polarization functions [9,13,14]. This is due to cancellation of the intra-atomic correlation correction to the first-order exchange energy (repulsive) and the interaction of higher instantaneous multipoles (attractive) [13,9]. Both these effects are disregarded in the SCF–DISP approximation.

The aim of this paper is to elucidate the role of higher polarization functions in calculations of the dispersion energy for a model rare-gas dimer, Ne_2, in the region of the van der Waals minimum. We use the partial wave expansion as described in ref. [9] which is evaluated through the h–h term. We believe that the results presented here will provide a better understanding of the attractive part of the Ne–Ne poten-

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tial. They also shed new light on the reliability of limited-basis-set calculations of the dispersion effect by means of both the perturbation and supermolecule variational methods.

2. Theory

The dispersion energy between two spherically symmetric systems A and B may be written in the form of the partial wave expansion [9]

$$E^{(2)}_{\mathrm{disp}} = \sum_{l_a, l_b}^{\infty} E(l_a, l_b), \tag{1}$$

$$E(l_a, l_b) = \sum_{i_a, j_b}^{\mathrm{occ}} \sum_{m=-l<}^{l<} E(i_a \to l_a, j_b \to l_b, m), \tag{2}$$

where $i_a(j_b)$ denote the sets of quantum numbers $n_a L_a M_a (n_b L_b M_b)$ of occupied orbitals of A(B) and l_a, l_b are angular quantum numbers. Explicit expressions for pair dispersion energies $E(i_a \to l_a, j_b \to l_b, m)$ were given in ref. [9]. For two Ne atoms, $L_a, L_b \leqslant 1$ and the multipole expansion of $E(i_a \to l_a, j_b \to l_b, m)$ is a polynomial in R^{-1}, the asymptotically leading term of which may be found from the formula [9]

$$E(n_a L_a M_a \to l_a, n_b L_b M_b \to l_b, m) R^{-2(k_a+k_b+1)}, \tag{3}$$

where

$$k_x = l_x, \qquad \text{for } L_x = 0;$$

$$= l_x + 2\delta_{0,l_x} + 2\delta_{1,l_x} - 1, \qquad \text{for } L_x = 1.$$

Knowledge of (3) is necessary to reorganize the partial wave expansion in such a way that subsequent terms are varying asymptotically as subsequent even powers of R^{-1} [9]:

$$E^{(2)}_{\mathrm{disp}} = \sum_{n=6,8,10,\ldots} E(n), \tag{4}$$

where

$$E(n) = \sum_{i_a, j_b}^{\mathrm{occ}} \sum_{l_a, l_b}^{2(k_a+k_b+1)=n} E(i_a \to l_a, j_b \to l_b) \tag{5}$$

and k_a and k_b are given by (3).

Since, in the region of the van der Waals minimum, pair dispersion interactions including the 2s orbital are an order of magnitude smaller than the $2p_a$–$2p_b$ interactions, it is expedient here to use a different partitioning of $E^{(2)}_{\mathrm{disp}}$:

$$E^{(2)}_{\mathrm{disp}} = \sum_{n=6,8,10,\ldots}^{\infty} \tilde{E}(n). \tag{6}$$

$$\tilde{E}(n) = \sum_{l_a, l_b} E(l_a, l_b),$$

$$2(l_a + l_b + 2\delta_{0,l_a} + 2\delta_{1,l_a} + 2\delta_{0,l_b} + 2\delta_{1,l_b} - 1) = n. \tag{7}$$

The sum in eq. (7) is over the l_a, l_b for which $E(2p_a \to l_a, 2p_b \to l_b)$ varies asymptotically as R^{-n}, i.e. as if the asymptotic behaviour of $E(l_a, l_b)$ were determined by the $2p_a$–$2p_b$ dispersion interaction. This is not true only if l_a and/or $l_b = 1$. In this case, $E(i_a \to l_a, j_b \to l_b)$ for i_a and/or $i_b = 2s$ provide the asymptotically leading contributions. This inconsistency will become serious only at larger distances, since $\tilde{E}(8)$ and $\tilde{E}(10)$ include terms of the order of R^{-6}. For $n > 10$, $E(n) = \tilde{E}(n)$.

3. Analysis of the partial wave expansion of $E^{(2)}_{\mathrm{disp}}$ for Ne_2

By using the method described in ref. [9], the variant with the Epstein–Nesbet zero-order Hamiltonian, the values of $E(nL_a \to l_a, nL_b \to l_b)$ have been calculated for R = 5.0, 5.5, 6.0 and 7.0 a_0, nL_a, nL_b = 1s, 2s and 2p, and l_a, l_b = 0, 1, 2, 3, 4 and 5. Throughout the calculations, Gaussian orbitals with spherical harmonics for angular parts were used. The occupied orbitals were represented as in ref. [9]. The basis set used to expand the dispersion function is displayed in table 1. The ATMOL integral package [15] and INTACT [16] were used to calculate integrals and dispersion energies, respectively.

The values of individual $E(l_a, l_b)$ and $\tilde{E}(n)$ are shown in table 2. All $E(n)$ for $n \leqslant 12$ are complete. For $n > 12$, the following terms are missing: i–d for n = 14; i–f, i–p and j–d for n = 16; i–g, j–f, j–p and k–d for n = 18. The asymptotically leading interactions of instantaneous multipoles to which a particular $E(l_a, l_b)$ (strictly speaking $E(2p_a \to l_a, 2p_b \to l_b)$, cf. section 2) may be related are also indicated.

Table 2 does not contain explicitly terms including s orbitals. They are always allowed for together with

Table 1
The exponents of GTOs used to expand the dispersion function

Type of GTO	Exponents(a_0^{-2})		
1s	0.15	0.30	0.06
2p [a)]	0.1	0.3088	0.704
3d [a)]	1.12	0.32	
4f [b)]	0.9	0.225	
5g [c)]	0.2		
6h [d)]	0.17		

a) The same as in ref. [9].
b) Chosen so as to maximize the value of $E(2p_a \to d_a, 2p_b \to f_b)$.
c) Chosen so as to maximize the value of $E(2p_a \to d_a, 2p_b \to g_b)$.
d) Chosen so as to maximize the value of $E(2p_a \to d_a, 2p_b \to h_b)$.

d orbitals (which are marked by a tilde). They must not be neglected, but it has been found that they are very well reproduced solely by the spherical combinations of Cartesian Gaussians [9] ‡. In this work, since we have used Gaussians multiplied by spherical harmonics, separate s orbitals had to be added.

It is important to estimate the accuracy of the calculation of individual terms. It has previously been found [9] and confirmed here that two polarization

‡ In ref. [9], where two spherical combinations of d orbitals were present in the basis set, additional s orbitals gave negligible contributions. This has led to the misleading comment that if l_a or $l_b = 0$, then $E(l_a, l_b)$ is negligible.

Table 2
Individual partial wave components $E(l_a, l_b)$ and the total dispersion energy. $\tilde{d}$ stands for s + d. R in a_0, energies in 10^{-5} hartree

$l_a - l_b$	Multipole [a)] interaction	$E(l_a, l_b)$			
		$R = 5.0$	$R = 5.5$	$R = 6.0$	$R = 7.0$
$\tilde{d}-\tilde{d}$	$E(6)$ = DD	41.9494	23.5871	13.8365	5.3700
2 × ($\tilde{d}$–p)	DQ	8.0054	4.1298	2.2354	0.7453
2 × ($\tilde{d}$–f)	DQ	11.4687	5.5861	2.8056	0.7961
	$E(8)$ =	19.4741	9.7159	5.0410	1.5414
p–p	QQ	0.5984	0.2510	0.1165	0.0317
2 × (f–p)	QQ	1.5609	0.6864	0.3190	0.0785
f–f	QQ	1.2898	0.5738	0.2589	0.0567
2 × (g–$\tilde{d}$)	OD	2.6881	1.2708	0.5911	0.1319
	$E(10)$ =	6.1372	2.7820	1.2805	0.2988
2 × (g–p)	OQ	0.4848	0.1955	0.0833	0.0166
2 × (g–f)	OQ	0.6792	0.3207	0.1460	0.0288
2 × (h–d)	HD	0.8567	0.4133	0.1901	0.0375
	$E(12)$ =	2.0207	0.9295	0.4194	0.0829
g–g	OO	0.0558	0.0347	0.0191	0.0044
2 × (h–p)	HQ	0.2287	0.0846	0.0328	0.0056
2 × (h–f)	HQ	0.2305	0.1159	0.0544	0.0106
	$E(14)$ =	0.5150	0.2352	0.1063	0.0206
2 × (h–g)	$E(16)$:HO	0.0267	0.0189	0.0118	0.0033
h–h	$E(18)$:HH	0.0030	0.0024	0.0017	0.0006
sum		70.1261	37.2710	20.7022	7.3176

a) D = dipole, Q = quadrupole, O = octupole, H = hexadecapole.

functions for a given symmetry, with optimized exponents, reproduce a particular term with ≈1% error. Calculations including only one polarization function of a given symmetry are less accurate. For example, use of only one orbital to calculate the d–f and f–f terms yields respectively 92% and 87%, of the result obtained with two f orbitals. Exactly the same conclusion was found to be valid for the d–g and g–g terms. The above remarks allow us to estimate the error in $E^{(2)}_{\mathrm{disp}}$ due to the fact that only one g and one h function was used. The resulting error in the total $E^{(2)}_{\mathrm{disp}}$ is ranging from 0.7% at $R = 5a_0$ to 0.3% at $R = 7a_0$.

The values of $E^{(2)}_{\mathrm{disp}}$ in table 2 are also in error because the partial wave expansion has been truncated and includes only terms for $l_a, l_b < 6$. One can see that the series (6) is well convergent and the largest of the missing terms, the d–i term, corresponds to dipole–2^5-pole type and belongs to $\tilde{E}(14)$.

Since dipole–octupole and dipole–hexadecapole terms provide ≈45% of $\tilde{E}(10)$ and $\tilde{E}(12)$, respectively (independent of R), it is reasonable to assume that the dipole–2^5-pole term yields also about half of the total $\tilde{E}(14)$. This assumption and perusal of the h–g and h–h terms leads to the conclusion that higher than h orbitals would give a contribution approximately equal to 0.7% at $R = 5a_0$ and 0.2% at $R = 7a_0$ of $E^{(2)}_{\mathrm{disp}}$.

From the above discussion of the errors of individual $E(l_a, l_b)$ and of the error of truncation of the series (6), one may conclude that, as far as basis-set limitations are concerned, the reported values of $E^{(2)}_{\mathrm{disp}}$ may be in error by 1.5% at $R = 5a_0$ to 0.5% at $R = 7a_0$.

Finally, we should comment on the error which results from the inadequacy of the method of calculation of the dispersion energy. Since the procedure is based on the Epstein–Nesbet zero-order Hamiltonian ("state-energy denominators") [17], not only is the intra-atomic correlation neglected but the definition of the procedure itself reveals certain drawbacks [18,9]. On the other hand, the procedure gives van der Waals coefficients for He_2 close to the experimental ones [18], and this would also seem to be valid for Ne_2 [9]. Nevertheless, since the van der Waals coefficients for Ne_2 are not known with sufficient accuracy [19], we are unable to analyse this error.

From the point of view of supermolecule calculations of the dispersion effects, it is important to know what accuracy can be achieved if a basis set consists of orbitals up to a given angular quantum number. Assuming that the total result in table 2 is exact, one can find that inclusion of only up to d, up to f and up to g orbitals provides (in the range 5.0–7.0 a_0) 72.1% to 84.0%, 92.5% to 96.7%, and 98.1% to 99.2%, respectively, of $E^{(2)}_{\mathrm{disp}}$. At the van der Waals minimum, the error in the interaction energy may be substantially larger, as the repulsive contribution cancels about half of the dispersion effect. For instance, lack of higher than f functions, assuming that no fortuitous cancellation of errors occurs, may in approximately 10% and 25% error in the interaction energy at $R = 6a_0$ and $5.5a_0$, respectively. Unfortunately, since one cannot use the partial wave expansion within the supermolecule approach, a basis set should include all necessary polarization functions at the same time and hence would rapidly become prohibitively large. At present, the only remedy is to carry out so-called "balanced" calculations, i.e. based on the more-or-less precise knowledge of possible cancellations of different errors, both basis set and conceptual. An example of such a method is the ICF (interaction correlated fragments) method of Liu and McLean [20].

4. Interaction potential for Ne_2

Recently, a few accurate semi-empirical potentials for Ne_2 have been proposed and proved to be very successful in reproducing a variety of dilute-gas properties of Ne (cf. ref. [3] and references therein). Particularly interesting from the point of view of comparison with ab initio perturbation calculations is the so-called exchange Coulomb (XC) potential model, the attractive long-range part ΔE_c of which consists of a sum of the first three terms of the multipole expansion for the second-order dispersion energy multiplied by a proper damping function:

$$\Delta E_c = -(C_6/R^6 + C_8/R^8 + C_{10}/R^{10})f(R). \qquad (8)$$

The values of individual C_n, in particular if they are allowed to vary within the bounds of Tang et al. [19], may be only approximately compared with calculated ab initio values. On the other hand, the total ΔE_c effect is expected to model accurately the net attractive effect. According to symmetry-adapted perturbation theory, ΔE_c accounts for the second- and higher-order

Table 3
Interaction energy (in 10^{-5} hartree) and its components between Ne atoms, from ab initio and semi-empirical results

	$R(a_0)$			
	5.0	5.5	6.0	7.0
$\Delta E^{\mathrm{int}}_{\mathrm{SCF}}$ [a]	74.01	21.76	6.38	0.54
$E^{(2)}_{\mathrm{disp}}$	−70.13	−37.27	−20.70	−7.32
$E_{\mathrm{ex-disp}}$ [a]	3.92	1.22	0.38	0.04
$E^{(2)}_{\mathrm{disp}} + E_{\mathrm{ex-disp}}$	−66.21	−36.05	−20.32	−7.27
$\Delta E^{\mathrm{int}}_{\mathrm{SCF}} + E^{(2)}_{\mathrm{disp}} + E_{\mathrm{ex-disp}}$	7.80	14.29	−13.95	−6.74
E_{SC}(XC-2) [b]	84.98	25.26	7.51	0.66
ΔE_{C} [b]	−66.37	−35.68	−20.24	−7.44
E_{int}(XC-2) [b]	18.61	−10.42	−12.73	−6.78
E_{SR}(XC-2) + $E^{(2)}_{\mathrm{disp}} + E_{\mathrm{ex-disp}}$	18.77	−10.79	−12.81	−6.61

[a] From ref. [9]. [b] Calculated from ref. [3].

dispersion energies damped by overlap and exchange dispersion effects [9]. We have compared in table 3 the values of ΔE_{c} for the best of the XC potentials, XC-2, with the values of $E^{(2)}_{\mathrm{disp}}$ from this work quenched by the exchange dispersion effect, $E_{\mathrm{ex-disp}}$, calculated in ref. [9]. One can see a remarkably good agreement between $E^{(2)}_{\mathrm{disp}}$ and ΔE_{c}. We should keep in mind here that an approximate algorithm for $E^{(2)}_{\mathrm{disp}}$ has been used and that we neglected the third-order dispersion contribution which must be accounted for by ΔE_{c}. On the other hand, the semi-empirical character of the XC-2 potential does not permit its precise division into well-defined terms. Consequently, a detailed analysis of a small discrepancy between ΔE_{c} and $E^{(2)}_{\mathrm{disp}}$ would not be meaningful.

We have also calculated the total interaction energy in the SCF–DISP approximation modified by adding $E_{\mathrm{ex-disp}}$ [9]:

$$E_{\mathrm{int}} \approx \Delta E^{\mathrm{int}}_{\mathrm{SCF}} + E^{(2)}_{\mathrm{disp}} + E_{\mathrm{ex-disp}}\,, \qquad (9)$$

where $\Delta E^{\mathrm{int}}_{\mathrm{SCF}}$ is the SCF interaction energy.

It is seen from table 3 that eq. (9) provides too deep a curve and even the position of the minimum is shifted to shorter R. The conclusion is that $\Delta E^{\mathrm{int}}_{\mathrm{SCF}}$ underestimates the repulsive part of the Ne_2 potential. Indeed, if one replaces $\Delta E^{\mathrm{int}}_{\mathrm{SCF}}$ in eq. (7) by the short-range part of the XC-2 potential, E_{SR}(XC-2), the values of the interaction energy are very close to those of the XC-2 potential (cf. table 3).

On the basis of the results for the He dimer [13,2], one can expect that the difference E_{SR}(XC-2) − $\Delta E^{\mathrm{int}}_{\mathrm{SCF}}$ is mainly due to the intra-atomic correlation correction to the first-order interaction energy. If so, this contribution would be far from negligible.

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