

Correlated van der Waals coefficients for dimers consisting of He, Ne, H₂, and N₂

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(Received 3 March 1987; accepted 13 January 1988)

Time-dependent coupled Hartree–Fock frequency-dependent polarizabilities have been corrected for true correlation effects by means of many-body perturbation theory. Polarizabilities have been computed for the monomers He, Ne, H₂, and N₂ through second order in the correlation potential. With these polarizabilities as input the van der Waals coefficients of all possible dimers have been obtained by the use of the Casimir–Polder relation.

I. INTRODUCTION

The second order properties of a molecule describe the response of the molecule to an external field. Experimentally, these properties can be obtained by bringing the molecule into the field and by measuring the term that is quadratic in the field parameters.

In this paper we are concerned with the interaction of molecules with multipolar electric fields.¹ In that case the second order properties are multipole polarizabilities. Multipole polarizabilities are of importance to phenomena such as absorption, refraction, light scattering, and intermolecular forces. Our main interest in these polarizabilities arises from this last property, i.e., from their relationship to van der Waals dispersion coefficients, which contribute to the intermolecular long range forces between van der Waals molecules.² When we know the polarizabilities as a function of imaginary frequencies we can calculate the dispersion coefficients with the help of the Casimir–Polder integral.³

Nowadays, *static* second order properties can be calculated with good precision, by the use of the finite field method.⁴ Correlation effects, which can contribute significantly to the property values,^{5,6} can be incorporated by the finite field many-body perturbation theory^{7–12} [MBPT(*n*), where *n* is the highest order considered in the correlation potential] or by the finite field configuration interaction (CI) method, which, when truncated to single and double CI (SD-CI), should be corrected for unlinked clusters¹³ by use of the Davidson–Siegbahn formula.^{14,15}

For *dynamic* properties, reasonable results can be obtained by the use of the time-dependent coupled Hartree–Fock (TDCHF) method,¹⁶ but this method only incorporates “apparent” correlation (or self-consistency) effects,¹⁷ while true correlation effects often are by no means negligible. Still, there is a great need for the computation of accurate dispersion coefficients and their anisotropies. This is especially true for the higher ones (*C*₈ and *C*₁₀), which are very difficult to obtain from experimental sources, and which play an important role in the description of intermolecular interactions.

True correlation effects in frequency-dependent polarizabilities can be obtained by the solution of the first order (in the external field) perturbation equation in a CI basis. This method was initiated by Nesbet¹⁸ and applied recently by

Visser, Wormer, and Jacobs to the systems He, H₂, N₂, O₂, and Ne.¹⁹ These workers truncated the CI basis at the SD-CI level and except for the two-electron systems He and H₂, for which this method is in effect a full CI perturbation calculation, their results were rather disappointing. An analysis of their results, with the help of the diagrammatic techniques commonly used in MBPT methods, was published in a recent paper,²⁰ which we will henceforth refer to as paper I. In this paper we showed, that, just as in the case of the finite field SD-CI method for static properties, for dynamic second order properties truncation at the SD-CI level introduces unlinked clusters, which can be canceled by adding triple excitations to the basis (the SDT-CI method), or by explicitly correcting for these clusters. We derived approximate Davidson-type formulas for these corrections.

As large scale SDT-CI calculations are very expensive, and the Davidson-type corrections, which seemed to be quite promising after some test calculations on neon, showed some erratic behavior for N₂, we will follow here an alternative route. The correlation effects described by all linked diagrams through second order in the correlation potential will be computed in the algebraic approximation,^{21–23} i.e., by expression of the problem in a finite orbital basis. These true correlation contributions will be added to the results of the TDCHF method. As will be seen in this paper, the results thus obtained are in better agreement with the existing accurate data than the uncorrected TDCHF values. This not only means that true correlation effects are not at all negligible, but also that they can be obtained reliably by the present method.

In Sec. II we will briefly survey the theory and basic equations. We will also present the correlation diagrams that were used, but in a somewhat different way than we did in paper I. The computational aspects are given in Sec. III. In Sec. IV we will present the results of the computations on the helium and neon atoms and the linear molecules H₂ and N₂. As little or no data are available on polarizabilities for imaginary frequencies no reliable comparison is possible. Therefore, we will only present our results for frequency zero (i.e., the static polarizabilities), for which comparison with literature values is possible. The accuracy of the dispersion coefficients will give an indication of the reliability of the polarizabilities over the whole range of imaginary frequencies. As stated above, our method extends the TDCHF approach,

and—especially for the isotropic properties—we will see that it yields better results. Therefore, we expect our C_8 and C_{10} values to be the most accurate values obtained to date. We believe this especially for the C_{10} coefficient of Ne, because we have calculated it with a basis set containing g orbitals, which are necessary to obtain a reliable dipole–octupole contribution. Finally in Sec. V a brief summary and the conclusions will be presented.

II. THEORY

As the general theory has already been given in paper I, only the most important formulas will be reviewed here and no derivations will be given. Note, however, that the diagrammatic representation of the formulas in this paper is according to the Hugenholtz convention, whereas in the previous paper we employed Brandow diagrams.¹³

We consider an N -electron molecule in a monochromatic electric field¹ of frequency $\omega/2\pi$. The Hamiltonian of this system in the second quantization formalism is

$$H = \sum_{i,j} \langle i|h + W \cos(\omega t)|j \rangle X_i^\dagger X_j + \frac{1}{2} \sum_{i,j,k,l} \langle ij|v|lk \rangle X_i^\dagger X_j^\dagger X_k X_l, \quad (1)$$

where X_i and X_i^\dagger are the well known operators which annihilate, respectively create, an electron in spin-orbital i , and $W \cos(\omega t)$ is the interaction of the electrons with the time-dependent external field. The operator W is a Hermitian one-electron multipolar operator,

$$W = \sum_m (-1)^m V_{-m}^l Q_m^l, \quad (2)$$

where Q_m^l is the usual 2^l -pole operator, and the parameters V_m^l determine the strength and direction of the field. Using Wick's theorem,¹³ we can write H in normal product form as

$$H_N = H - E_0 = H_N^{(0)} + (W_0 + W_N) \cos(\omega t) = F_N + V_N + (W_0 + W_N) \cos(\omega t), \quad (3)$$

where E_0 is the energy of the Fermi vacuum $|\Phi_0\rangle$, which we will take as our energy zero, F_N is the Fock operator in normal product form and V_N is the electronic correlation potential. We approximate the solution of the Schrödinger equation by solving the zeroth and first order equation of

time-dependent perturbation theory

$$H_N^{(0)} |\Psi^{(0)}\rangle = E^{(0)} |\Psi^{(0)}\rangle, \quad (4)$$

$$[H_N^{(0)} - E^{(0)} + \omega] |\Psi^{(1)}(\omega)\rangle = (\Delta E^{(1)} - W_N) |\Psi^{(0)}\rangle, \quad -\infty < \omega < +\infty, \quad (5)$$

where

$$\Delta E^{(1)} = \frac{\langle \Psi^{(0)} | W | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} - W_0 = \frac{\langle \Psi^{(0)} | W_N | \Psi^{(0)} \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} \quad (6)$$

is the correlation contribution to the permanent multipole moments of the molecule. Our aim is to compute the frequency-dependent polarizability, which is proportional to minus the second order energy

$$\alpha(\omega) \approx -E^{(2)}(\omega) = -\frac{\langle \Psi^{(0)} | W_N | \Psi^{(1)}(\omega) \rangle + \langle \Psi^{(0)} | W_N | \Psi^{(1)}(-\omega) \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle}. \quad (7)$$

For imaginary frequencies α takes a similar form, with all ω substituted by $i\omega$. In order to obtain an expansion of the zeroth and first order wave function in terms of the correlation potential V_N , we define the projectors:

$$P = |\Phi_0\rangle \langle \Phi_0|, \quad Q = 1 - P, \quad (8)$$

and the reduced resolvent

$$R(\omega) = \frac{Q}{Q(F_N + \omega)Q}, \quad (9)$$

one can then derive (cf. paper I)

$$E^{(0)} = \langle \Phi_0 | V_N Q | \Psi^{(0)} \rangle, \quad (10)$$

$$|\Psi^{(0)}\rangle = (P + Q) |\Psi^{(0)}\rangle = |\Phi_0\rangle - \sum_{k=0}^{\infty} [R(0)(E^{(0)} - V_N)]^k R(0) V_N |\Phi_0\rangle, \quad (11)$$

$$|\Psi^{(1)}(\omega)\rangle = \sum_{k=0}^{\infty} [R(\omega)(E^{(0)} - V_N)]^k \times R(\omega)(\Delta E^{(1)} - W_N) |\Psi^{(0)}\rangle. \quad (12)$$

Using Eqs. (10)–(12) and only retaining terms to second order in the correlation potential V_N , we get for the first term of Eq. (7), after expansion of its denominator

$$\begin{aligned} \frac{\langle \Psi^{(0)} | W_N | \Psi^{(1)}(\omega) \rangle}{\langle \Psi^{(0)} | \Psi^{(0)} \rangle} &= \langle \Phi_0 | W_N R(\omega) W_N \langle \Phi_0 | V_N R^2(0) V_N | \Phi_0 \rangle + W_N R^2(\omega) W_N \langle \Phi_0 | V_N R(0) V_N | \Phi_0 \rangle \\ &\quad - W_N R(\omega) W_N + W_N R(\omega) V_N R(\omega) W_N - W_N R(\omega) V_N R(\omega) V_N R(\omega) W_N \\ &\quad - V_N R(0) W_N R(\omega) W_N R(0) V_N + V_N R(0) W_N R(\omega) W_N + W_N R(\omega) W_N R(0) V_N \\ &\quad - W_N R(\omega) W_N R(0) V_N R(0) V_N - V_N R(0) V_N R(0) W_N R(\omega) W_N \\ &\quad - W_N R(\omega) V_N R(\omega) W_N R(0) V_N - V_N R(0) W_N R(\omega) V_N R(\omega) W_N | \Phi_0 \rangle. \end{aligned} \quad (13)$$

A corresponding expression for the second term of Eq. (7) is obtained in the same way. We give a diagrammatic representation of this expression in terms of prototypes of Hugenholtz diagrams (Fig. 1), where we follow the conven-

tion of Paldus and Čížek¹² by letting the time flow from right to left. A prototype represents a class of Hugenholtz diagrams that differ only by the orientation of the Fermion lines. Resolvents are only shown explicitly—by vertical

lines—when they appear squared. In this figure the resolvents are decomposed as a sum of one-, two-, and three-particle resolvents. For each prototype, firstly all possible orientations of the Fermion lines are considered and then each Hugenholtz diagram thus obtained is brought into one-to-one correspondence with a Brandow (antisymmetric) diagram, which we evaluate algebraically. The advantage of this sequence of operations over the one used in paper I, is that it is easier to systematically generate all the Hugenholtz diagrams than to generate all the Brandow diagrams directly. Furthermore it is essential to get the orientations of the Fermion lines in the Hugenholtz diagrams before the conversion to Brandow diagrams, in order to get all terms correctly.

In Fig. 1, we have divided the diagrams in different groups, each giving a successive level of approximation. Diagram (a) is a representation of the uncoupled Hartree-Fock (UCHF) approximation. Addition of diagrams (b) and (c) and higher order diagrams of the same type yields the representation of the singly excited CI (SECI) approximation.

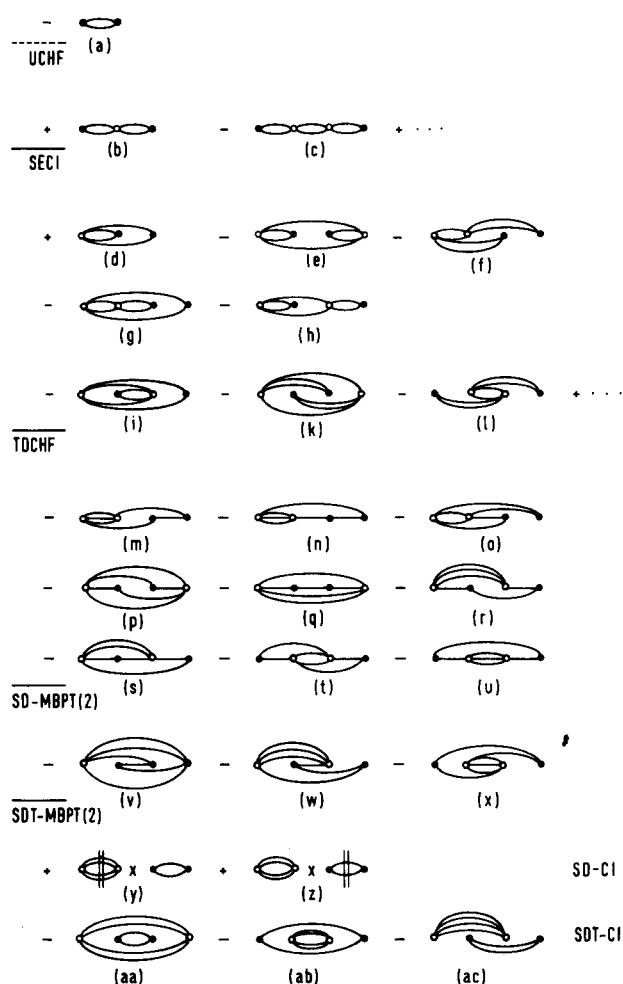


FIG. 1. Prototypes of Hugenholtz diagrams, giving the contributions to the frequency-dependent polarizability through second order in the correlation potential. The solid dot nodes with two outgoing lines represent the external field, the open dot nodes with four outgoing lines represent the correlation potential. Resolvents between solid dots are ω dependent. The mirror images of diagrams d, f-i, m-o, r, s, w, and ac are not shown, but must be included.

The type three diagrams (d-l) are characterized by the fact that in each diagram the different two-electron nodes, representing the correlation potential, are interconnected by exactly two Fermion lines, and that each of the two W_N nodes is connected to only one two-electron node. This type of diagram summed to infinite order, and added to the SECI diagrams, yields the TDCHF (or random phase) approximation. As we solve the TDCHF problem directly (see Ref. 16), we do not compute diagrams (a-l) explicitly and sum this class of diagrams to infinite order. Diagrams (m-ac) are the true correlation diagrams. In these diagrams the nodes representing the external potential W_N are interconnected with two different nodes. Diagrams (m-u) contain only singly and doubly excited intermediate states whereas diagrams (v-x) contain also triply excited intermediate states. Finally, diagrams (y-ac) are the unlinked diagrams. As we saw in paper I, diagrams (y) and (z) are canceled by diagrams (aa-ac), except for those terms in diagrams (y) and (z), in which the two disconnected diagrams have a spin-orbital label in common. These are not canceled by terms in diagrams (aa-ac) because in the latter diagrams they are exclusion principle violating (EPV). Throughout this paper we will follow the somewhat unfortunate standard nomenclature and refer to these terms in diagrams (y) and (z) as "EPV" terms, although they do not violate the exclusion principle, which is why we shall consistently use the quotes in referring to these terms. It is good to stress that the "EPV" terms are non-EPV—and hence must be included on theoretical grounds—and that they are of nonnegligible size, so that for practical reasons, too, they must be considered. We find it convenient to compute the so-called "EPV" terms of diagrams (y) and (z) via the true EPV terms of diagrams (v-x), which is possible because of the well known result that these EPV terms are equal in magnitude to the disconnected "EPV" terms.

In summary, our method—which we refer to as SDT-MBPT—consists of an exact solution of the TDCHF equations and the calculation of the true correlation effects through second order in the correlation potential.

III. COMPUTATIONAL DETAILS

The theory of Sec. II has been applied to the atoms helium and neon and to the molecules hydrogen and nitrogen. In all cases a basis of tesseral harmonic Gaussian-type atomic orbitals was used. The SCF ground state calculations, the computation of the one-electron matrices of the multipole operators, and the two- and four- index transformations were carried out by the ATMOL4 set of programs.²⁴ The dynamic polarizabilities on the TDCHF level of approximation were computed with the TDCHF package of programs, developed in this institute.²⁵ The molecular bond distances used were the vibrationally averaged equilibrium values of 1.449 (H_2) and 2.068 bohr (N_2). For helium and hydrogen we used the uncontracted basis sets given by Meyer²⁶ (see Table I). For nitrogen, the basis set *B* of Visser, Wormer, and Stam¹⁶ was used. We used four different basis sets for the description of the neon atom. Basis set I is the basis of Visser *et al.*¹⁶ Basis set II is essentially the uncontracted D^* basis of Diercksen and Sadlej,²⁷ but as mentioned above we use tes-

TABLE I. Basis set information.^a

He	(10s, 5p, 3d, 2f) ^b
H ₂	(6s, 3p, 3d) on each H + (1p, 2f) at H ₂ center ^b
N ₂	(12s, 7p, 3d, 2f/6s, 5p, 3d, 2f) ^c
Ne	Basis I: (11s, 7p, 2d, 1f/7s, 5p, 2d, 1f) ^c
	Basis II: (12s, 8p, 3d, 3f) ^d
	Basis III: basis II + 1 g orbital ($\alpha = 0.2$)
	Basis IV: basis II + 2 g orbitals ($\alpha = 0.1$ and $\alpha = 0.4$)

^a All orbitals are tesseral harmonic GTOs.

^b Reference 26.

^c Reference 16.

^d The same exponents as the *D** basis of Diercksen (Ref. 27), but here defined as tesseral harmonic GTOs and not as Cartesian GTOs.

seral harmonic GTOs, whereas these authors used Cartesian GTOs, so their set contains three more *s*-type orbitals and three more *p*-type orbitals. Basis set III is the same as basis set II, with an added *g* orbital of exponent $\alpha = 0.2$. This exponent maximizes the static finite field SCF octupole polarizability of Ne. Finally basis set IV is the same as basis set

II, with two added *g* orbitals of exponents $\alpha = 0.4$ and $\alpha = 0.1$.

Since we merge essentially two correlation methods, special care has to be taken with regard to the cancellation of the EPV terms. If one would evaluate all (linked) diagrams of Fig. 1 explicitly, the EPV terms would be treated correctly; however, since we calculate the diagrams (a-1) and the related higher order ones by solution of the TDCHF equations,¹⁶ which, of course, does not give any EPV terms, we have to analyze the diagrams (*m*-*x*) in order to ascertain that all the EPV terms are canceled. It appears that this is the case, except for the EPV terms of diagram (o), which would have to cancel against the EPV versions of diagrams (f) and (g). So the EPV terms of diagram (o) were evaluated explicitly, and the MBPT results were corrected for these terms. This correction is by no means negligible.

To obtain van der Waals dispersion coefficients from dynamical polarizabilities, we use Eqs. (32) and (44) of Ref. 16 which are valid for *S*-state atoms and homonuclear diatomics and which we will repeat here for easy reference. [Notice that Eq. (32) contains an error.²⁸ The phase factors $(-1)^{m_A}$ and $(-1)^{m_B}$ must be left out.]

$$C_{l_A l'_A l'_B l'_B}^{L_A L_B L} = (-1)^{l_A + l'_A} \left[(2l_A + 2l_B + 1)(2l'_A + 2l'_B + 1) \binom{2l_A + 2l_B}{2l_A} \binom{2l'_A + 2l'_B}{2l'_A} \right]^{1/2} \cdot$$

$$\times (2L_A + 1)(2L_B + 1)(2L + 1) \begin{Bmatrix} l_A & l'_A & L_A \\ l_B & l'_B & L_B \\ l_A + l_B & l'_A + l'_B & L \end{Bmatrix}$$

$$\times \begin{pmatrix} l_A + l_B & l'_A + l'_B & L \\ 0 & 0 & 0 \end{pmatrix} \sum_{m_A} \begin{pmatrix} l_A & l'_A & L_A \\ m_A & -m_A & 0 \end{pmatrix} \sum_{m_B} \begin{pmatrix} l_B & l'_B & L_B \\ m_B & -m_B & 0 \end{pmatrix} X_{m_A m_B}^{l_A l'_A l'_B l'_B}, \quad (14)$$

where

$$X_{m_A m_B}^{l_A l'_A l'_B l'_B} = \frac{1}{2\pi} \int_0^\infty \alpha_{l_A m_A, l'_A - m_A}(i\omega) \alpha_{l_B m_B, l'_B - m_B}(i\omega) d\omega. \quad (15)$$

The expression between braces is a *9j* symbol and the three quantities between parentheses to the right of the *9j* symbol are *3j* symbols. The integral is known as the Casimir-Polder integral,³ which we compute numerically, using a Gauss-Chebyshev integration scheme. To show how we do this we notice that the polarizability components $\alpha_{lm, l'm'}(i\omega)$, which appear in the integral are real functions in which ω appears quadratically, so that the integrand is a symmetric function in ω . We introduce the short hand notation

$$I = \int_0^\infty f(\omega) d\omega = \frac{1}{2} \int_{-\infty}^\infty f(\omega) d\omega \quad (16)$$

for Eq. (15). By the successive substitutions

$$\begin{aligned} \omega &= \cot(\alpha), \\ \alpha &= \arccos(x) \end{aligned} \quad (17)$$

we transform this integral to

$$I = \frac{1}{2} \int_{-1}^1 \frac{f[\cot[\arccos(x)]]}{1-x^2} \frac{dx}{\sqrt{1-x^2}}. \quad (18)$$

The volume element and the integration limits correspond with the Gauss-Chebyshev quadrature.²⁹ Hence

$$I \approx \frac{\pi}{2N} \sum_{i=1}^N \frac{f[\cot(\phi_i)]}{\sin^2(\phi_i)}, \quad (19)$$

where

$$x_i = \cos(\phi_i) \text{ and } \phi_i = \frac{2i-1}{2N} \pi, \quad i = 1, \dots, N. \quad (20)$$

Because of the symmetry properties of the trigonometric functions, it is sufficient to compute only $N/2$ gridpoints for *N* even, so that the final formula for the integral becomes

$$I \approx \frac{\pi}{N} \sum_{i=1}^{N/2} \frac{f[\cot(\phi_i)]}{\sin^2(\phi_i)}. \quad (21)$$

To determine the number *N* we computed the *C*₆ of neon in the smallest basis for different values of *N* (see Table II). Since a four digit accuracy is enough we used the value *N* = 20 in all cases.

TABLE II. Convergence of Gauss–Chebyshev quadrature for $(\text{Ne})_2$ in basis I.

N	C_6
8	6.6934
16	6.6529
20	6.6520
30	6.6517
40	6.6517

We conclude this section with some remarks on the MBPT program, which contains two steps. Input to the program are the two-electron integrals and the multipole integrals, both over molecular orbitals, as well as the TDCHF or SECI eigenvectors and eigenvalues. The first step consists of a reordering of the two-electron integrals. In the second step the 48 Brandow diagrams originating from the Hugenholtz prototypes ($m-x$) and their mirror images are computed and added to the TDCHF values of the dynamic polarizabilities. The algorithm is (two-electron) integral driven. The “EPV” terms of diagrams (y) and (z) can be computed optionally by this program. Finally, there are built-in options to compute the polarizabilities at the uncoupled Hartree–Fock or singly excited CI level.

IV. RESULTS AND DISCUSSION

As we saw in Sec. II our SDT-MBPT method yields frequency-dependent polarizabilities in which all apparent correlation effects are summed to infinite order in the correlation potential, because we take the TDCHF results as the basis of our calculations. Furthermore true correlation effects are computed to second order. The main advantage of the present approach over the CI-perturbation method, truncated at the SD-CI level, is that unlinked clusters are not included, but the price one has to pay is that the correlation contributions are not accounted for after second order in the correlation potential.

We will now discuss the behavior and accuracy of this method for the helium and neon atom, and the linear molecules hydrogen and nitrogen. We compare the values with TDCHF results and accurate literature values as far as they are available. We will end this section by briefly considering the mixed dimers consisting of these monomers.

A. He and H_2

Two-electron systems are the simplest systems where correlation effects are present. Since full CI calculations on these systems are still computationally feasible, we obtain near exact results by the SD-CI perturbation method.¹⁹ In Table III we have collected the results of the computed static polarizabilities and dispersion coefficients of helium, together with TDCHF results, full CI results, and other selected literature values. For this two-electron atom the TDCHF method already yields good results, indicating that the true correlation effects are small in this case.

The difference between the results of the full CI method and our SDT-MBPT results is of course due to the neglect of

TABLE III. Results for He and $(\text{He})_2$ (in a.u.).

	TDCHF ^a	SDT-MBPT	FULL CI ^b	LIT ^c
α_1	1.322	1.354	1.385	1.383
α_2	2.316	2.372	2.445	2.443
α_3	9.941	10.22	10.60	10.61
C_6	1.375	1.431	1.463	1.461
C_8	13.12	13.66	14.11	14.11
C_{10}	168.4	175.8	183.2	183.6

^a Reference 16.

^b Reference 19.

^c Explicitly correlated results. Reference 30.

diagrams that are higher than second order in the correlation potential. Both the TDCHF method and the SDT-MBPT method yield values that lie consistently below the full CI and above the uncoupled Hartree–Fock results. In other words, the apparent as well as the true correlation effects on the polarizabilities are positive for the He atom.

For all the helium properties considered, SDT-MBPT gives results that are in closer agreement with the full CI values¹⁹ than the TDCHF method.¹⁶ The percentage difference between TDCHF and full CI results in the polarizabilities range from -4.5% to -6.2% . For SDT-MBPT these numbers are from -2.2% to -3.6% . In the case of the dispersion coefficients we see that the differences between TDCHF and full CI vary between -6.0% and -8.1% , whereas the differences between SDT-MBPT and full CI are from -2.2% to -4.0% . So, the addition of the true correlation contributions ($m-x$) of Fig. 1 to the TDCHF results reduces the errors by about 50%.

In the case of the H_2 molecule (Table IV), we see that all TDCHF and SDT-MBPT values lie above the full CI results, in contrast to the helium case. The improvement due to the

TABLE IV. Results for H_2 and $(\text{H}_2)_2$ (in a.u.).

	TDCHF	SDT-MBPT	FULL CI ^a	LIT ^b
$\alpha_{10,10}$ ^c	6.812	6.962	6.745	6.771
$\alpha_{11,11}$	4.787	4.819	4.760	4.728
$\alpha_{20,20}$	19.30	19.35	...	19.07
$\alpha_{21,21}$	18.14	18.12	...	18.05
$\alpha_{22,22}$	15.04	14.87	...	14.55
$\alpha_{30,30}$	141.4	138.8	...	124.8
$\alpha_{31,31}$	136.7	133.9	...	129.6
$\alpha_{32,32}$	125.3	122.1	...	121.1
$\alpha_{33,33}$	108.2	105.0	...	99.7
$\bar{\alpha}_1$ ^d	5.462	5.533	5.422	5.409
$\Delta\alpha_1$ ^e	2.026	2.143	1.985	2.043
$\bar{\alpha}_2$	17.13	17.07	16.87	16.85
$\bar{\alpha}_3$	126.0	123.0	119.2	117.9
C_6^{000}	12.30	12.62	12.15	12.12
C_8^{000}	217.8	219.5	212.6	213.3
C_{10}^{000}	4976	4922	4741	4741

^a Reference 19.

^b Reference 26.

^c Notation α_{l_m, l'_m} .

^d $\bar{\alpha}_l = 1/(2l+1) \sum_m \alpha_{l_m, l_m}$.

^e $\Delta\alpha_1 = \alpha_{10,10} - \alpha_{11,11}$.

consideration of true correlation effects is not very pronounced for this simple molecule. For some properties (notably the components of the dipole polarizability) the SDT-MBPT results even deviate more from the full CI values than the TDCHF results, although both sets of values are very accurate (errors < 3.2%). This shows that the expansion [Eq. (13) and higher terms] of the polarizability in powers of the correlation potential does not always converge monotonically. Indeed, one of the well known disadvantages of the perturbation-type methods, as compared to variational methods, is this nonmonotonic behavior.

The difference with full CI values for the isotropic polarizabilities lies between + 1.2% and + 3.2% in the case of SDT-MBPT and between + 0.7% and + 5.7% for TDCHF. However, the SDT-MBPT dipole anisotropy shows a fairly large discrepancy (8%). Since the dipole anisotropy is computed as the difference between the parallel and the perpendicular component of the dipole polarizability tensor and since the accuracy in these two components is not the same, the error in the difference between these components accumulates, causing this relatively large error.

The results for the dispersion coefficients are consistent with those of the polarizabilities. Indeed, we see that in the case of C_6 and C_8 the TDCHF values are somewhat better. On the other hand, SDT-MBPT yields better results for C_{10} than TDCHF, which is in line with the fact that the SDT-MBPT quadrupole and octupole polarizabilities are in better agreement with the full CI results than the corresponding TDCHF values.

B. Ne

For the ten-electron system neon it is not possible at this moment to perform full CI perturbation calculations, so that we do not have good benchmark calculations for this system. TDCHF calculations on neon by Visser, Wormer, and Stam¹⁶ show large (12%–15% errors) discrepancies with accurate empirical values, indicating that for neon true correlation effects are of considerable importance.

To have a comparison with the TDCHF results of Visser *et al.* we first performed calculations in the same basis (basis I). We have also as a reference our earlier SDT-CI calculations,²⁰ which were obtained by the solution of the first order equation, Eq. (5), in a CI basis consisting of singly, doubly, and selected triply excited states and in the same AO basis. In Table V we have collected the different results. We see that our present SDT-MBPT dipole polarizability has the same value (2.659 a.u.) as our earlier SDT-CI result. When we compare this with the semiempirical value of 2.668 a.u. by Langhoff and Karplus,³¹ which is well established, we see that the inclusion of true correlation greatly improves the TDCHF values, reducing the error from -12.4% to -0.3%. Similarly, our value of C_6 (6.65 a.u.) lies well above the TDCHF value and very close to the result of 6.55 a.u. of Starkschall and Gordon.³⁶ Comparing this with the SDT-CI value of 6.44 a.u. we see that our present C_6 lies + 3.3% higher, although the static dipole polarizability is the same, indicating that the functional dependence of the polarizability on the frequency is not quite the same in both methods [cf. the Casimir-Polder integral Eq. (15)].

TABLE V. Polarizabilities of Ne and dispersion coefficients of $(\text{Ne})_2$ in four different bases (in a.u.).

	TDCHF ^a					
	α_1^b	α_2^c	α_3^d	C_6^e	C_8^f	C_{10}^g
Basis I	2.337	5.930	15.57	5.39	68.3	727
Basis II	2.371	6.350	18.23	5.50	73.0	817
Basis III	2.371	6.350	30.83	5.50	73.0	1119
Basis IV	2.371	6.350	30.80	5.50	73.0	1122
	SDT-MBPT					
	α_1^b	α_2^c	α_3^d	C_6^e	C_8^f	C_{10}^g
Basis I	2.659	6.897	18.50	6.65	87.6	965
Basis II	2.677	7.362	21.89	6.67	91.8	1069
Basis III	2.678	7.371	37.67	6.68	91.9	1487
Basis IV	2.680	7.382	37.87	6.69	92.2	1492

^a Reference 16.

^b Lit: 2.668 semiempirical estimate (Ref. 31); 2.658 SDT-CI (Ref. 20).

^c Lit: 7.48 FF-MBPT in basis D^* (Ref. 27); 7.73 CEPA (Ref. 32); 6.826 SDT-CI (Ref. 20).

^d Lit: 30.37 MBPT (Ref. 33); 34.27 numerical CHF (Ref. 34).

^e Lit: 6.43 (Ref. 35); 6.551 (Ref. 36); 6.87 (Ref. 37); 6.44 SDT-CI (Ref. 20).

^f Lit: 76.0 (Ref. 37); 83.8 SDT-CI (Ref. 20).

^g Lit: 1100. (Ref. 37).

Turning to the quadrupole polarizability α_2 , we see that our SDT-MBPT value (6.897 a.u.) is a good deal higher than the TDCHF result of 5.930 a.u., and a little above our earlier SDT-CI perturbation result of 6.826 a.u.²⁰ It is still much smaller, however, than the literature value of 7.48 a.u. of Diercksen and Sadlej,²⁷ who used the finite field MBPT method to fourth order in the correlation potential, and than the value of 7.73 a.u. obtained by Reinsch and Meyer³² with the CEPA method. As we remarked in the introduction, the finite field methods yield accurate static polarizabilities, and we believe the α_2 value of Diercksen and Sadlej to be very accurate, and our result for α_2 and C_8 to be too low in this basis.

To improve the comparison we repeated our calculations with basis set II, which has the same exponents as the D^* basis of Diercksen and Sadlej, but is defined in a basis of tesseral harmonic GTOs, whereas these workers used Cartesian GTOs. In basis II our dipole polarizability increases only slightly (+ 0.7%), just as the C_6 dispersion coefficient (+ 0.3%), which shows that the dipole properties are already near their basis set limit in basis I. The increase in the quadrupole polarizability is more drastic (+ 6.7%) and the difference with the finite field MBPT result is decreased from -7.8% to -1.6%. The remaining difference with the result of Diercksen and Sadlej can be explained partly by the greater flexibility in their basis, due to the extra s and p orbitals, and partly by third and fourth order correlation effects. We conclude that basis I is of sufficient quality to describe the dipole properties, but with respect to the quadrupole properties, basis I is not yet complete.

Our value (91.9 a.u.) of C_8 obtained in basis II lies + 21% above the estimate of 76.0 a.u. of Tang, Norbeck,

and Certain,³⁷ but is still below their upper bound of 96.4 a.u. Because Tang *et al.* used the quadrupole polarizability value 6.42 a.u. computed by Doran,³³ which according to Diercksen and Sadlej,²⁷ Reinsch and Meyer,³² and our own computations, is much too low, we expect that the true C_8 value should lie well above theirs and so we believe our present value to be more reliable.

Inspection of the octupole polarizability α_3 shows that there is an increase in the value of this property when we go from TDCHF to SDT-MBPT and within the SDT-MBPT approach by the transition from basis I to basis II. Still, even in basis II the value of α_3 is much lower than the literature values (30.37 a.u.) of Doran³³ and (34.27 a.u.) of McEachran, Stauffer, and Greita.³⁴ This is to be expected since bases I and II do not contain g orbitals, which are necessary for a proper description of the dynamic octupole polarizability. Consequently, for the C_{10} dispersion coefficient, which depends on this polarizability, we need a basis which supports $s \rightarrow f$ and $p \rightarrow g$ excitations. As reliable results for quantities that depend on octupole transitions cannot be expected in bases I and II, we repeated the calculations in basis III (which is basis II with one g orbital added).

At this point it is perhaps good to remark that static octupole polarizabilities of S -state atoms, obtained by the TDCHF approach (which for infinitesimal static fields is equivalent to the finite field SCF method) can only increase upon addition of one or more g orbitals to the basis. The same is true for correlation methods, if we may assume that the g orbital(s) do not correlate the ground state of the S state atom. This can be proved rigorously by application of the Hylleraas variational principle.³⁸ The assumption that the g orbitals do not correlate the ground state is justified to a large extent for the diffuse g orbital(s) necessary to describe the octupole polarizabilities.

To test further the validity of this assumption we performed an additional calculation in basis II with a split g orbital added (basis IV). We see in Table V that addition of one or two g orbitals has only a minor effect on the dipole and quadrupole properties, but there is a substantial increase in the octupole polarizability (+ 72%) upon addition of one g orbital. A basis with two g orbitals increases this value only very little. Because of its dependence on the dipole–octupole contribution, the C_{10} value also increases substantially (+ 39%) in basis III. Again the result in basis IV shows only a minor increase. The octupole polarizability and the C_{10} dispersion coefficient seem to require only one diffuse g orbital in the basis. To our knowledge, this is the first *ab initio* calculation of the C_{10} dispersion coefficient of neon (in the algebraic approximation) that includes g orbitals in the basis. Therefore, our C_{10} is likely to be the most accurate value available at present.

C. N_2

Not many accurate data exist for the N_2 molecule and the $(N_2)_2$ dimer. There are experimental data on the rotationally averaged dipole polarizability and dipole anisotropy from several different groups^{40–42} and a semiempirical estimate of the isotropic and anisotropic C_6 coefficients, due to Langhoff, Gordon, and Karplus.⁴³ Recently Cernusak,

TABLE VI. Comparison of TDCHF and MBPT for N_2 and $(N_2)_2$ in (a.u.).

	TDCHF ^a	SDT-MBPT	LIT
$\alpha_{10,10}$ ^b	14.805	15.460	14.78 ^e
$\alpha_{11,11}$	9.697	9.979	10.26 ^e
$\alpha_{20,20}$	91.78	96.76	91.60 ^f
$\alpha_{21,21}$	94.45	99.27	94.97 ^f
$\alpha_{22,22}$	44.26	44.45	26.96 ^f
$\bar{\alpha}_1$ ^c	11.40	11.81	11.77 ^e
$\Delta\alpha_1$ ^d	5.11	5.48	4.52 ^e
$\bar{\alpha}_2$	73.84	76.84	67.09 ^f
C_6^{000}	71.46	75.63	73.8 ^g
γ_6^{022h}	0.2627	0.2892	0.237 ^g
γ_6^{220}	0.0066	0.0078	0.0054 ^g
γ_6^{222}	0.0177	0.0208	0.014 ^g
γ_6^{224}	0.1911	0.2246	0.155 ^g
C_8^{000}	2351	2489	...
γ_8^{022}	1.2885	1.3966	...
γ_8^{220}	0.0192	0.0223	...
γ_8^{222}	-0.0642	-0.0805	...
γ_8^{224}	0.4479	0.5350	...
γ_8^{044}	-0.0560	-0.0522	...
γ_8^{42}	-0.0011	-0.0011	...
γ_8^{244}	-0.0029	-0.0030	...
γ_8^{246}	-0.0601	-0.0601	...

^a Reference 16.

^b Notation $\alpha_{lm,l'm'}$.

^c $\bar{\alpha}_l = 1/(2l+1) \sum_m \alpha_{lm,lm}$.

^d $\Delta\alpha_1 = \alpha_{10,10} - \alpha_{11,11}$.

^e Experimental, Ref. 40.

^f Finite field SD-MBPT(4), Ref. 39.

^g Semiempirical estimate, Ref. 43.

^h $\gamma_n^{L_1 L_2 L_3} = C_n^{L_1 L_2 L_3} / C_n^{000}$.

Diercksen, and Sadlej³⁹ published the components of the static quadrupole polarizability tensor—computed with the finite field MBPT method to fourth order in the correlation potential—but they state that their basis is not very well suited for the description of this property. The most extensive calculations of polarizabilities and dispersion coefficients seem to be those of Visser *et al.*,¹⁶ who used the TDCHF method and obtained reasonable results.

Since our N_2 basis does not contain g orbitals, we will restrict our attention to the dipole and quadrupole properties of N_2 (Table VI). Looking at the isotropic dipole polarizability we see that our SDT-MBPT result of 11.81 a.u. is very good, lying only + 0.4% above the experimental value of 11.76 a.u. This may be compared with the TDCHF value of 11.40 a.u., which is 3.1% below the experimental result. Both TDCHF and SDT-MBPT yield a dipole anisotropy which differs greatly ($\approx 20\%$) from the experimental result, and again the accumulation of errors, due to taking the difference between the parallel and the perpendicular component may be partly responsible for this error. Turning to the C_6 dispersion coefficient, we see that for the isotropic coefficient our SDT-MBPT value of 75.63 a.u. is somewhat better than the TDCHF value of 71.46 a.u., the differences with the

semiempirical estimate being + 2.4% and - 3.2%, respectively.

Not much can be said about the accuracy of the anisotropy of C_6 , because the semiempirical estimates are based on rather crude data. However, there is no reason why the errors in the computed values of these quantities would be smaller than the 20% error in the computed $\Delta\alpha_1$. One of the likely sources for this error is the AO basis. It is not impossible that the present 100-dimensional N_2 basis is not big enough to describe adequately these second order properties. Clearly much more work, experimentally and theoretically, is required to establish the anisotropy factors with greater precision than they are known at present.

For the quadrupole properties even less is known than for the dipole properties. According to Cernusak *et al.*³⁹ their value of 67.2 a.u. is too low. This agrees with the fact that our TDCHF and SDT-MBPT values are considerably higher. Judging by our experience with He, Ne, and H_2 we hope that for SDT-MBPT the error in the isotropic quadrupole polarizability will be less than 4%, although our N_2 basis is small in comparison to the bases used for these lighter systems.

To compare the different components of the quadrupole tensor obtained by Cernusak *et al.*³⁹ with our results, we transformed their Cartesian components to our convention

by the following formulas,

$$\begin{aligned}\alpha_{20,20} &= 3C_{zz,zz}, \\ \alpha_{21,21} &= 4C_{xz,xz}, \\ \alpha_{22,22} &= 4C_{xx,xx} - C_{zz,zz}.\end{aligned}\quad (22)$$

We see that Cernusak's values happen to agree very well with the results obtained by the TDCHF method, except for $\alpha_{22,22}$, for which they find a much lower value. Both our TDCHF and SDT-MBPT value are almost a factor of 2 higher than the result of Cernusak *et al.* Since this quantity depends very sensitively on the d and f orbitals, it may well be that this difference is indicative for the basis set dependence of these second order properties.

The TDCHF C_8 dispersion coefficients of Visser *et al.*¹⁶ are the only ones known to us. As in the case of the dipole properties and the quadrupole polarizability, our results lie about 5% above theirs. We expect our isotropic C_8 coefficient to be the more accurate one, since the present method is by design an improvement on the method of Visser *et al.*

D. Mixed dimers

When all necessary components of the dynamic polarizability tensors for a set of monomers are available, it is possible to compute the dispersion coefficients of the dimers con-

TABLE VII. Dispersion coefficients for mixed dimers (in a.u.) in SDT-MBPT approximation.^{a,b,c}

	He-Ne	He-H ₂	Ne-H ₂	He-N ₂	Ne-N ₂
C_6	3.075 ^d (2.724)	4.048 ^e (3.913)	8.441 ^a (7.473)	10.27 ^w (9.795)	21.75 ^{ab} (19.07)
γ_6^2	...	0.2252 ^h (0.2114)	0.2204 ^f (0.2055)	0.2801 ^t (0.2518)	0.2742 ^{ac} (0.2433)
C_8	36.01 ^e (31.25)	55.43 ⁱ (54.21)	135.4 ^g (119.6)	218.1 ^y (208.0)	509.9 (443.0)
γ_8^2	...	0.6649 ^k (0.6297)	0.5940 ^l (0.5676)	2.049 ^z (1.896)	1.880 (1.760)
γ_8^4	...	0.0260 ^j (0.0229)	0.0217 (0.0193)	-0.0690 ^{aa} (-0.0757)	-0.0576 (-0.0634)
C_{10}	522.0 ^f (439.7)	1005 ^m (996.2)	2681 ⁿ (2358)
γ_{10}^2	...	0.7745 ⁿ (0.7429)	0.7226 ^v (0.7007)
γ_{10}^4	...	0.0209 ^o (0.0132)	0.0189 (0.0124)
γ_{10}^6	...	0.0167 ^p (0.0161)	0.0128 (0.0126)

^a Between parentheses are TDCHF results.

^b The results of dimers containing Ne are all in basis IV.

^c $\gamma_n^L = C_n^{OL}/C_n^{OO}$.

^d (3.05-3.21) Ref. 37, (3.03-3.20) Ref. 47, 3.041 Ref. 35, 3.029 Ref. 48.

^e (28.2-37.2) Ref. 37, (28.3-37.0) Ref. 47.

^f (338-520) Ref. 37, (386-534) Ref. 47.

^g 4.030 Ref. 19, 4.018 Ref. 46.

^h 0.2099 Ref. 19, 0.2176 Ref. 46.

ⁱ 55.51 Ref. 19, 55.0 Ref. 46.

^j 0.6912 Ref. 19, 0.7014 Ref. 46.

^k 0.0156 Ref. 19, 0.0173 Ref. 46.

^l 1005 Ref. 19, 1025.3 Ref. 46.

^m 0.8138 Ref. 19, 0.7652 Ref. 46.

ⁿ 0.0251 Ref. 19, 0.0278 Ref. 46.

^o 0.0157 Ref. 19, 0.0056 Ref. 46.

^p 8.47 Ref. 44, 8.28 Ref. 43.

^q 0.2102 Ref. 44, 0.2258 Ref. 43.

^r 129.0 Ref. 44.

^s 0.5814 Ref. 44.

^t 2430 Ref. 44.

^u 0.5814 Ref. 44.

^v 10.21 Ref. 45, 10.22 Ref. 49.

^w 0.2258 Ref. 45.

^x 185.0 Ref. 45.

^y 1.087 Ref. 45.

^z -0.1350 Ref. 45.

^{aa} 21.8 Ref. 43.

^{ac} 0.2147 Ref. 43.

TABLE VIII. Dispersion coefficients for H₂-N₂ (in a.u.) in SDT-MBPT approximation.^{a,b}

	$n = 6$		$n = 8$	
C_n^{000}	30.54 ^c	(29.28)	771.7	(744.0)
γ_n^{022}	0.2981	(0.2741)	1.741	(1.594)
γ_n^{044}	...		-0.0777	(-0.0827)
γ_n^{202}	0.2339	(0.2199)	0.4470	(0.4244)
γ_n^{220}	0.0065	(0.0057)	0.0143	(0.0127)
γ_n^{222}	0.0174	(0.0153)	-0.0536	(-0.0447)
γ_n^{224}	0.1877	(0.1653)	0.3487	(0.3013)
γ_n^{242}	...		-0.0014	(-0.0014)
γ_n^{244}	...		-0.0036	(-0.0035)
γ_n^{246}	...		-0.0732	(-0.0721)
γ_n^{404}	...		0.0146	(0.0130)
γ_n^{422}	...		0.0003	(0.0002)
γ_n^{424}	...		0.0005	(0.0004)
γ_n^{426}	...		0.0141	(0.0117)

^a Values between parentheses are TDCHF results. Reference 16.

^b $\gamma_n^{L_1 L_2 L_3} = C_n^{L_1 L_2 L_3} / C_n^{000}$.

^c Lit 29.2 Ref. 43, 29.45 Ref. 49.

sisting of these monomers by the Casimir-Polder relation, Eq. (15). Visser *et al.*¹⁶ have published the dispersion coefficients for all mixed dimers containing He, Ne, H₂, and N₂ in the TDCHF approximation. Because the SDT-MBPT method yields better results than the TDCHF approach and also because our basis for neon (basis IV) is of higher quality than the basis they used (basis I) we judged it worthwhile to recompute these dispersion coefficients for all the mixed dimers. The results of these computations are collected in Tables VII and VIII.

Starting with the He-Ne dimer, we can compare our C_6 (3.075 a.u.) with the bounds (3.05–3.21 a.u.) determined by Tang, Norbeck, and Certain³⁷ and by Standard and Certain⁴⁷ (3.03–3.20 a.u.) from sum rules and Padé approximant techniques. Further literature values available are the C_6 coefficient (3.041 a.u.) of Leonard and Barker,³⁵ and of Kumar and Meath⁴⁸ (3.029 a.u.), obtained from pseudodipole oscillator strength distributions. These last authors claim an error of less than 1%. Notice that their value lies slightly below the lower bounds given by Tang *et al.* and by Standard and Certain. Our result for the C_6 coefficient lies just above those lower bounds and is in very good agreement with the two semiempirical values, lying +1.5% above the result of Kumar and Meath and +1.1% above the result of Leonard and Barker. The TDCHF value for C_6 lies -10% below the value of Kumar and Meath. So the improvement over the TDCHF approach is considerable.

Our C_8 coefficient (36.01 a.u.) lies close to the upper bound (37.2 a.u.) given by Tang *et al.* and Standard and Certain (37.0 a.u.). As we already discussed for the neon dimer, the calculations of these bounds were based on a value of the neon quadrupole polarizability, which, in all likelihood, is too low. This explains why our C_8 is close to the upper bounds.

The same holds for the C_{10} coefficient. Here the bounds of Standard and Certain bracket a higher value of C_{10} than the value of Tang *et al.*, because they used for neon the octu-

pole polarizability (34.27 a.u.) of McEachran *et al.*,³⁴ which is higher than the older value of Doran (30.37 a.u.). As our octupole polarizability is even higher than McEachran's, it is not surprising that we find a C_{10} which is close to the upper bound of Standard and Certain and above the upper bound of Tang *et al.* This high value for the octupole polarizability of neon and the C_{10} for He-Ne is mainly due to the inclusion of g orbitals in our neon basis.

Turning to the He-H₂ dimer, we see that the isotropic dispersion coefficients, obtained with the SDT-MBPT method, agree excellently with the full CI results¹⁹ and with the results of Meyer, Hariharan, and Kutzelnigg.⁴⁶ Although we would indeed expect from the polarizability data for He and H₂ that the dispersion coefficients of the dimer should be close to the full CI results, this agreement is too perfect, and somewhat fortuitous. Because the polarizability values for helium lie below and for H₂ they lie above the full CI values, these two errors cancel each other. But again, addition of true correlation improves the TDCHF results.

The differences between SDT-MBPT and full CI for the anisotropic coefficients are larger. As in the case of H₂ dimer it is debatable whether SDT-MBPT behaves better than TDCHF. The differences with full CI values for γ_n^2 for $n = 6, 8, 10$ are +7.3% (+0.7%), -3.8% (-8.9%), and -4.8% (-8.7%), respectively (between brackets are the TDCHF results). These errors are consistent with those found for the H₂ dimer, since the anisotropy in the dispersion is, of course, only due to the nonsphericity of H₂.

Next we look at the Ne-H₂ dimer. Except for the TDCHF calculations of Visser *et al.*,¹⁶ there are to our knowledge only the papers by Langhoff, Gordon, and Karplus⁴³ and by Tang and Toennies,⁴⁴ that report long range data on this system. Because our dipole polarizability for H₂ lies above the full CI value and the corresponding value for neon is rather accurate, we expect the C_6 result to lie a little above the exact value. Indeed, we find a value that is 1.8% higher than the one of Langhoff *et al.* Our result is also in good agreement with the value obtained by Tang and Toennies, their value being higher by only +0.5%.

However, the C_8 and C_{10} values show a larger difference with the results of Tang and Toennies, which is probably due to the inclusion of g orbitals in our neon basis. To test this, we computed the dispersion coefficients in basis II. The results are $C_6 = 8.43$ a.u., $C_8 = 135$ a.u., and $C_{10} = 2424$ a.u., which may be compared with the Tang and Toennies values of $C_6 = 8.47$ a.u., $C_8 = 129$ a.u., and $C_{10} = 2430$ a.u. We see that C_{10} , computed without g orbitals in the neon basis, agrees almost exactly with the value of Tang and Toennies.

The anisotropic coefficients given by Tang and Toennies and by Langhoff *et al.* are given in the LLM convention.¹⁶ To transform them to our LLL convention we used the following formula:

$$C_n^{OLL} = (-1)^L \sqrt{2L+1} C_n^{OLM} \quad (23)$$

[see Eq. (39) of Ref. 16]. The differences between our results and the results obtained by Tang and Toennies are larger than for the isotropic coefficients, while γ_6^2 of Langhoff *et al.* is close to our result.

Because we did not include g orbitals in the N₂ basis, so

that we cannot describe accurately the frequency-dependent octupole polarizability of N_2 , we restricted the computations for the dimers containing N_2 to the C_6 and C_8 coefficients.

For the He- N_2 dimer there is a semiempirical estimate of C_6 (10.22 a.u.), obtained from pseudodipole oscillator strength distributions, by Margoliash and Meath.⁴⁹ Other estimates for the isotropic C_6 (10.21 a.u.) and C_8 (185 a.u.) and their anisotropies are by Habitz, Tang, and Toennies,⁴⁵ who applied the method that was used by Tang and Toennies for Ne- H_2 . As their estimate of C_6 was too large as compared with the value of Margoliash and Meath, they scaled all their results. Finally there is a C_6 (10.3 a.u.) and γ_6^2 (0.2258) of Langhoff, Gordon, and Karplus.⁴³ Our result of 10.27 a.u. is in excellent agreement with the C_6 values of the different groups. Again there is a considerable improvement over the TDCHF value of 9.80 a.u. The result for γ_6^2 of Langhoff *et al.* and the scaled result of Habitz *et al.*, however, lies substantially lower than our result (−19%), whereas the unscaled result of Habitz *et al.* lies considerably above our result (+41%). Their scaled C_8 value is also substantially lower than our result whereas their unscaled result of 218 a.u. agrees exactly with our findings. Their unscaled γ_8^2 (1.901) lies also closer to our value than the scaled value, so this puts some doubt on the use of a C_6 -scaling factor for C_8 .

The only available data for Ne- N_2 are a semiempirical estimate of C_6 and γ_6^2 of Langhoff, Gordon, and Karplus⁴³ and TDCHF calculations of Visser *et al.*¹⁶ As we used a different Ne basis than Visser *et al.*, our TDCHF results differ slightly from theirs. Again there is an excellent agreement between our result for C_6 and the estimate of Langhoff *et al.*, much better than for TDCHF, but again their value of γ_6^2 lies about −21% below our result.

For H_2 - N_2 (Table VIII) the same trend is observable. Our isotropic C_6 coefficient (30.54 a.u.) agrees to within a few percent with the semiempirical estimate of Margoliash and Meath⁴⁹ (29.45 a.u.) and of Langhoff *et al.*⁴³ (29.2 a.u.). For the other coefficients, no other data are available, except the TDCHF values.

V. SUMMARY AND CONCLUSIONS

We have added to the TDCHF values of the frequency-dependent polarizabilities all true correlation contributions through second order in the correlation potential, including those that contain triply excited intermediate states. Using those corrected polarizabilities, we have computed dispersion coefficients. In all cases where comparison with experimental or accurate theoretical results is possible, the agreement is good, although the anisotropy in the dipole polarizability of the linear molecules H_2 and N_2 , which is difficult to compute accurately, still tends to be overestimated somewhat, just as in the TDCHF approach. In order to improve the accuracy of the computed anisotropy values for N_2 , it may be wise first to consider a larger and better AO basis than higher order correlation effects. The accuracy of the static isotropic polarizabilities is high, and the isotropic dispersion coefficients can be computed *ab initio* with an error of only a few percent. The addition of true correlation effects in general improves the values obtained by TDCHF,

especially for dimers containing helium or neon. For H_2 , however, where TDCHF gives already accurate results, there is no definite improvement, and higher than second order correlation must be considered, if more precision is desired.

ACKNOWLEDGMENTS

The authors wish to thank Dr. P. Knowles for the addition of a module for the computation of multipole integrals to the ATMOL4 package of programs. This investigation was supported in part by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

- ¹D. P. Craig and T. Thirunamachandran, *Adv. Quantum Chem.* **16**, 97 (1982).
- ²A. van der Avoird, P. E. S. Wormer, F. Mulder, and R. Berns, in *Topics in Current Chemistry* (Springer, Berlin, 1980), p. 1.
- ³H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948).
- ⁴H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.* **43**, S34 (1965).
- ⁵H. J. Werner and W. Meyer, *Mol. Phys.* **31**, 855 (1976).
- ⁶H. J. Werner and W. Meyer, *Phys. Rev. A* **13**, 13 (1976).
- ⁷H. P. Kelly, *Phys. Rev.* **131**, 684 (1963).
- ⁸H. P. Kelly, *Adv. Chem. Phys.* **14**, 129 (1969).
- ⁹J. Goldstone, *Proc. R. Soc. London Ser. A* **239**, 267 (1957).
- ¹⁰K. A. Brueckner, *Phys. Rev.* **97**, 1353 (1955).
- ¹¹D. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic, New York, 1972).
- ¹²J. Paldus and J. Cizék, *Adv. Quantum Chem.* **9**, 105 (1975).
- ¹³J. Paldus, *Diagrammatical Methods for Many-Fermion Systems*, Lecture Notes (University of Nijmegen, 1981).
- ¹⁴E. R. Davidson, in *The World of Quantum Chemistry*, edited by R. Daudel and B. Pullman (Reidel, Dordrecht, 1974).
- ¹⁵P. E. M. Siegbahn, *Chem. Phys. Lett.* **55**, 386 (1978).
- ¹⁶F. Visser, P. E. S. Wormer, and P. Stam, *J. Chem. Phys.* **79**, 4973 (1983).
- ¹⁷A. J. Sadlej, *J. Chem. Phys.* **75**, 320 (1981).
- ¹⁸R. K. Nesbet, *Phys. Rev. A* **14**, 1065 (1976).
- ¹⁹F. Visser, P. E. S. Wormer, and W. P. J. H. Jacobs, *J. Chem. Phys.* **82**, 3753 (1985).
- ²⁰P. E. S. Wormer and W. Rijks, *Phys. Rev. A* **33**, 2928 (1986).
- ²¹R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
- ²²S. Wilson and D. M. Silver, *Phys. Rev. A* **14**, 1949 (1976).
- ²³S. Wilson, in *Specialist Periodical Reports*, Vol. 4 of *Theoretical Chemistry* (Royal Society of Chemistry, London, 1981), p. 1.
- ²⁴V. R. Saunders and M. F. Guest, Daresbury Laboratory, Warrington, United Kingdom. P. Knowles, University of Cambridge, United Kingdom.
- ²⁵F. Visser, P. E. S. Wormer, and P. Stam, University of Nijmegen, The Netherlands.
- ²⁶W. Meyer, *Chem. Phys.* **17**, 27 (1976).
- ²⁷G. H. F. Diercksen and A. J. Sadlej, *Phys. Rev. A* **27**, 2795 (1983).
- ²⁸F. Visser, P. E. S. Wormer, and P. Stam, *J. Chem. Phys.* **81**, 3755 (1984).
- ²⁹M. Abramowitz and L. A. Stegun, *Handbook of Mathematical Functions* (U.S. GPO, Washington, D.C., 1968), p. 889.
- ³⁰A. J. Thakkar, *J. Chem. Phys.* **75**, 4496 (1981).
- ³¹P. W. Langhoff and M. Karplus, *J. Opt. Soc. Am.* **59**, 863 (1969).
- ³²E. A. Reinsch and W. Meyer, *Phys. Rev. A* **18**, 1793 (1978).
- ³³M. B. Doran, *J. Phys. B* **7**, 558 (1974).
- ³⁴R. P. McEachran, A. D. Stauffer, and S. Greita, *J. Phys. B* **12**, 3119 (1979).
- ³⁵P. J. Leonard and J. A. Barker, in *Theoretical Chemistry, Advances, and Perspectives*, edited by H. Eyring and D. Henderson (Academic, New York, 1975).
- ³⁶G. Starkschall and R. G. Gordon, *J. Chem. Phys.* **54**, 663 (1971).
- ³⁷K. T. Tang, J. M. Norbeck, and P. R. Certain, *J. Chem. Phys.* **64**, 3063 (1976).
- ³⁸S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974).

- ³⁹I. Cernusak, G. H. F. Diercksen, and A. J. Sadlej, *Chem. Phys.* **108**, 45 (1986).
- ⁴⁰G. R. Alms, A. K. Burham, and W. H. Flygare, *J. Chem. Phys.* **63**, 3321 (1975).
- ⁴¹N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. London Ser. A* **295**, 334 (1966).
- ⁴²K. Kerl, *Z. Phys. Chem.* **129**, 129 (1982).
- ⁴³P. W. Langhoff, R. G. Gordon, and M. Karplus, *J. Chem. Phys.* **55**, 2126 (1971).
- ⁴⁴K. T. Tang and J. P. Toennies, *J. Chem. Phys.* **68**, 5501 (1978).
- ⁴⁵P. Habitz, K. T. Tang, and J. P. Toennies, *Chem. Phys. Lett.* **85**, 461 (1982).
- ⁴⁶W. Meyer, P. C. Hariharan, and W. Kutzelnigg, *J. Chem. Phys.* **73**, 1880 (1980).
- ⁴⁷J. M. Standard and P. R. Certain, *J. Chem. Phys.* **83**, 3002 (1985).
- ⁴⁸A. Kumar and W. J. Meath, *Mol. Phys.* **54**, 823 (1985).
- ⁴⁹D. J. Margoliash and W. J. Meath, *J. Chem. Phys.* **68**, 1426 (1978).