PHYSICAL REVIEW A VOLUME 33, NUMBER 5 MAY 1986

Analysis of the correlation effects in molecular second-order time-dependent properties: Application to the dynamic polarizabilities of the neon atom and the dispersion coefficients of the Ne_2 dimer

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(Received 30 December 1985)

A diagrammatic analysis is presented of the electronic correlation in second-order time-dependent molecular properties. It is shown that the solution of the first-order time-dependent perturbation equation in a configuration-interaction (CI) basis will give considerable errors, when the basis is truncated at the singly and doubly excited-state CI level and unperturbed orbitals are used. This is due to the occurrence of unlinked clusters for which correction formulas are derived in the present paper. The theory is illustrated by calculations on the Ne atom and the Ne_2 dimer. Cluster-corrected polarizabilities and dispersion coefficients are compared with values obtained in large CI bases containing triply excited states.

I. INTRODUCTION

Molecular properties can be measured by bringing a molecule into an external field and determining the interaction energy of the molecule and the field. This energy may be expanded as a Taylor series in the field parameters, and if the external field is weak compared to the internal fields of the molecule, the expansion is quickly convergent. This usually being the case, one commonly considers only the terms linear and quadratic in the field. The linear term is proportional to *a first-order property*, and the quadratic term is proportional to *a second-order property*. The first-order properties are permanent properties of the molecule, and the second-order properties describe its response to the applied field. In this paper we are concerned with interactions of molecules with multipolar electric fields.[1] In that case the first-order properties are permanent multipole moments and the second-order properties are multipole polarizabilities.

Great strides have been made in the computation of second-order properties during the last two decades. Especially *static* properties can be calculated nowadays with very good precision. A convenient and reliable method is the *finite-field method*.[2] Application of the finite-field procedure to the HF (Hartree-Fock) equations yields the same second-order properties as those obtained by the CHF (coupled HF) method,[3] and the RPA (random-phase approximation) method.[4] From the point of view of diagrammatic MBPT (many-body perturbation theory) these three methods can be described by stating that they sum the so-called bubble diagrams to infinite order in the correlation potential V.[5] From the point of view of CHF theory no correlation is involved, only a self-consistent solution of the first-order perturbed HF equation is required. This is why Sadlej[6] calls these self-consistency effects "apparent correlation."

Also "true" correlation effects[6] can be obtained by finite-field methods. One can, for instance, apply MBPT and use the one-electron Hamiltonian (Fock operator plus the external field) as the zeroth-order Hamiltonian. The correlation potential V can then be accounted for in a few low orders by the usual summations over linked diagrams.[7] This approach can be analyzed in terms of double perturbation theory, where the field-free HF equations constitute the zeroth-order problem and where V and the external field are both treated perturbationally. This shows that finite-field MBPT is equivalent to a double perturbation theory in which the external field is "dressed" to infinite order by bubble diagrams.[8]

A similar distinction exists for finite-field CI (configuration interaction) methods in which the orbitals are, or are not, relaxed in the external field. If the CI basis is constructed from field-free orbitals , and if the basis is restricted to singly and doubly excited states (SDCI), the second-order properties turn out to be not very accurate. The reason for this is twofold. In the first place one misses part of the self-consistency effects, because only bubble diagrams with intermediate summations over singles and doubles are accounted for. Secondly, and more importantly, the second-order energy is contaminated by unlinked clusters, which are already second order in V. This can be shown by the same techniques as will be used in this paper. If, on the other hand, a SDCI computation is based on finite-field orbitals, self-consistency effects are accounted for to infinite order in V, and the first unlinked cluster that appears is the one that can be computed by the Davidson-Siegbahn formula.[9,10] Hence the second-order property can be easily corrected and reliable results are obtained.

The importance of orbital relaxation for second-order properties computed by the coupled-cluster (CC) method has been pointed out by Sekino and Bartlett.[11] In the CC method the problem caused by unperturbed orbitals is not the appearance of unlinked clusters, of course, but the fact that high excitations are needed for obtaining reliable results.[11]

The situation is not so favorable for *dynamic (time-dependent)* properties. Although fairly good results can be obtained by the TDCHF (time-dependent CHF) method (see, e.g., Ref. 12) true correlation effects are often important and are difficult to calculate. To a large extent this difficulty is due to the fact that there is no finite-field method that procures time-dependent orbitals. It is conceivable that the TDCHF method can be extended to yield second-order perturbed orbitals, but to date this has not been attempted. An additional problem is that the orbitals will depend on the strength and the frequency of the field. So, even if perturbed orbitals could be calculated, it would have to be done for many frequencies, which would make the correlation calculations very expensive, because they would require a four-index transformation for each frequency.

For the time being it is therefore inevitable to employ unperturbed orbitals. One can use these in double perturbation theory, in the manner pioneered by Kelly,[13] or in time-dependent CC theory for which Dalgaard and Monkhorst[14] have developed a formalism. We have chosen to describe the zeroth- and first-order time-dependent PT equations in a CI basis, and to solve these equations exactly. This way one obtains first- and second-order properties that are of infinite order in the correlation potential. The CI approach was initiated by Nesbet[15] and applied recently by Visser, Wormer, and Jacobs[16] to He, H_2, N_2, O_2, and Ne.

The zeroth-order equation in the CI approach to time-dependent properties is the ordinary CI equation and about its solution a vast literature is in existence. The solution of the first-order equation does not belong to the standard repertoire of quantum chemistry. Visser *et al.* solved the problem by an *ab initio* computation of Cauchy moments (moments of negative power of a multipole oscillator strength distribution) followed by a Padé approximant representation of the dynamic (frequency-dependent) polarizabilities.[17]

The advantage of the CI approach over the double perturbation approach of Kelly is that the method is in principle exact. And indeed, in cases small enough to be amenable to a full CI treatment nearly exact results have been obtained.[16] In practice, however, it is often necessary to truncate the CI basis at the SDCI level. As is well-known the zeroth-order energy is then contaminated by unlinked cluster contributions. One of the main purposes of this paper is to demonstrate that also second-order dynamic properties are contaminated by unlinked clusters. As a matter of fact, the use of unperturbed orbitals together with the truncation at the SDCI level introduces two types of unlinked clusters which are second-order in the correlation potential, and especially one of them gives a sizable contribution to the frequency-dependent polarizabilities. Furthermore it will be proved that these clusters cancel against terms that occur if the CI basis is extended to include triples, thus at the SDTCI level the results are markedly improved.

This paper is based on an analysis of the zeroth- and first-order equation by Rayleigh-Schrödinger perturbation theory.[18] Explicit formulas will be derived for the first two unlinked clusters that appear in SDCI dynamic properties, thus enabling us to correct for their effects. As a quantitative illustration of the theory results are presented for the dipole and quadrupole polarizabilities of the neon atom, together with the van der Waals constants C_6 and C_8 of the dimer. A comparison with results obtained in a SDTCI basis and with literature values shows that the SDCI properties are improved greatly and that a reliable calculation of correlated dynamic properties is possible by the SDCI perturbation method corrected for unlinked clusters, at least for closed-shell molecules.

II. THEORY

Consider an N-electron molecule in a monochromatic multipolar electric field[1] of frequency $\omega/2\pi$. Let its Hamiltonian be

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

where $X_i^\dagger$ and X_j are the usual fermion creation and annihilation operators, h is the kinetic energy plus nuclear attraction operator, v is the electron-electron repulsion and $W\cos(\omega t)$ is the interaction of the electrons with the time-dependent external field. The summations run over all molecular orbitals. Assuming that the molecule is in a closed-shell state, we distinguish occupied (hole) and virtual (particle) orbitals. The former will be designated by Greek letters $\alpha,\beta,\ldots$, and the latter by Latin letters $a,b,\ldots$. By the use of Wick's theorem the Hamiltonian can be written in normal product form with respect to the Fermi vacuum[19] $|\Phi_0\rangle$,

$$H_N := H - E_0 = F_N + V_N + (W_0 + W_N)\cos(\omega t) \ . \tag{2}$$

The following definitions apply:

$$E_0 := \sum_{\alpha} \langle \alpha \,|\, h \,|\, \alpha \rangle + \tfrac{1}{2} \sum_{\alpha,\beta} \langle \alpha\beta \,|\, v(1-P_{1,2}) \,|\, \alpha\beta \rangle \ , \tag{3}$$

$$F_N := \sum_{i,j} \langle i \,|\, f \,|\, j \rangle N[X_i^\dagger X_j] \ , \tag{4}$$

$$\langle i \,|\, f \,|\, j \rangle := \langle i \,|\, h \,|\, j \rangle + \sum_{\alpha} \langle i\alpha \,|\, v(1-P_{1,2}) \,|\, j\alpha \rangle \ , \tag{5}$$

$$V_N := \tfrac{1}{2} \sum_{i,j,k,l} \langle ij \,|\, v \,|\, lk \rangle N[X_i^\dagger X_j^\dagger X_k X_l] \ , \tag{6}$$

$$W_0 := \sum_{\alpha} \langle \alpha \,|\, W \,|\, \alpha \rangle \ , \tag{7}$$

$$W_N := \sum_{i,j} \langle i \,|\, W \,|\, j \rangle N[X_i^\dagger X_j] \ . \tag{8}$$

Henceforth we take the energy E_0 of the Fermi vacuum as our energy zero and consider H_N only.

Preferably we would partition the Hamiltonian in Eq. (2) such that all one-electron terms constitute the zeroth-order Hamiltonian. For the reasons stated in the Introduction, this is not feasible in the case of time-dependent fields, however, and therefore we start by solving the *time-independent* Hartree-Fock problem

$$f \,|\, \phi_i \rangle = \epsilon_i \,|\, \phi_i \rangle \tag{9}$$

in order to obtain the molecular orbitals ϕ_i and orbital energies ϵ_i. The operator f is defined by Eq. (5).

The solution of the Schrödinger equation is then approximated by means of time-dependent perturbation theory, i.e., by solving the zeroth- and first-order equation[20]

$$H_N^{(0)}\,|\Psi^{(0)}\rangle = E^{(0)}\,|\Psi^{(0)}\rangle\ , \tag{10}$$

$$(H_N^{(0)}-E^{(0)}+\omega)\,|\Psi^{(1)}(\omega)\rangle = (\Delta E^{(1)}-W_N)\,|\Psi^{(0)}\rangle\ , \tag{11}$$

where

$$H_N^{(0)} := F_N + V_N \tag{12}$$

and

$$\Delta E^{(1)} := \frac{\langle\Psi^{(0)}\,|\,W\,|\,\Psi^{(0)}\rangle}{\langle\Psi^{(0)}\,|\,\Psi^{(0)}\rangle} - W_0\ . \tag{13}$$

The second-order energy

$$E^{(2)}(\omega) = \frac{\langle\Psi^{(0)}\,|\,W_N\,|\,\Psi^{(1)}(\omega)\rangle + \langle\Psi^{(0)}\,|\,W_N\,|\,\Psi^{(1)}(-\omega)\rangle}{\langle\Psi^{(0)}\,|\,\Psi^{(0)}\rangle} \tag{14}$$

equals the negative of the frequency-dependent polarizability. In the derivation of the perturbation equations (10) and (11) use is made of the orthogonality condition

$$\langle\Psi^{(0)}\,|\,\Psi^{(k)}\rangle = 0,\quad k=1,2\ . \tag{15}$$

Furthermore, we shall apply the normalization conditions

$$\langle\Phi_0\,|\,\Phi_0\rangle = 1\ , \tag{16}$$

$$\langle\Phi_0\,|\,\Psi^{(0)}\rangle = 1\ . \tag{17}$$

The following orthogonality condition holds strictly and automatically if the perturbation W possesses a symmetry different from the ground state, which is always the case for atoms. If Φ_0 and $\Psi^{(0)}$ have the same symmetry as W and $\Psi^{(1)}$, Eq. (15) requires an orthogonalization of $\Psi^{(1)}$ to $\Psi^{(0)}$, and hence $\Psi^{(1)}$ receives a small[21] component along Φ_0, and the following equation does not hold strictly:

$$\langle\Phi_0\,|\,\Psi^{(k)}\rangle = 0,\quad k\geqq 1\ . \tag{18}$$

Below we shall discuss the solution of Eq. (10) and (11) and illustrate the contributions to the respective wave functions and energies graphically. To that end it is convenient to define the projector on the Hartree-Fock ground state

$$P := |\Phi_0\rangle\langle\Phi_0| \tag{19}$$

and the projector on its orthogonal complement (the Q space)

$$Q := 1-P\ . \tag{20}$$

Furthermore it is useful to define a frequency-dependent reduced resolvent

$$R(\omega) := \frac{Q}{Q(F_N+\omega)Q}\ . \tag{21}$$

Since $R(\omega)$ does not depend on V_N, we see that this is a Rayleigh-Schrödinger—type resolvent. Because the set of all singly, doubly , . . . , N-fold excited states spans the Q space, and because these excited states are eigenstates of F_N, the resolvent can be expressed as a sum of one-, two-, . . . , and N-particle resolvents, thus

$$R(\omega) = R_1(\omega)+R_2(\omega)+\cdots+R_N(\omega)\ . \tag{22}$$

Here the k-particle resolvent is given by

$$R_k(\omega) = \sum_{\alpha_1,\alpha_2,\ldots,\alpha_k}\ \sum_{a_1,a_2,\ldots,a_k} \frac{\hat{C}^{a_1,a_2,\ldots,a_k}_{\alpha_1,\alpha_2,\ldots,\alpha_k}\,|\Phi_0\rangle\langle\Phi_0|\,(\hat{C}^{a_1,a_2,\ldots,a_k}_{\alpha_1,\alpha_2,\ldots,\alpha_k})^{\dagger}}{(\epsilon_{a_1}-\epsilon_{\alpha_1})+\cdots+(\epsilon_{a_k}-\epsilon_{\alpha_k})}\ , \tag{23}$$

where the k-fold excitation operator is

$$\hat{C}^{a_1,a_2,\ldots,a_k}_{\alpha_1,\alpha_2,\ldots,\alpha_k} := \frac{1}{k!}N\left[\prod_{l=1}^{k} X^{\dagger}_{a_l}X_{\alpha_l}\right]\ . \tag{24}$$

It is easily proved that

$$R_k(\omega)R_l(\omega) = \delta_{k,l}R_k(\omega)^2\ , \tag{25}$$

where the squared resolvent has an appearance similar to the resolvent itself [Eq. (23)], with a squared sum of one-electron transition energies in the denominator.

A. The zeroth-order equation

In order to establish the notation we briefly consider the solution of the zeroth-order problem, Eq. (10). It is perhaps good to stress that in practice we describe this equation in a basis of singly and doubly excited states, and obtain the lowest roots by a standard iterative procedure.[22] The following analysis will exhibit what the correlation contributions are to the SDCI wave function and energy thus obtained. This analysis is closely related to the one of Bartlett and Shavitt.[23]

Following Löwdin[18] in his derivation of Rayleigh-Schrödinger perturbation theory we partition Eq. (10). Using

$$\langle\Phi_0\,|\,V_N\,|\,\Phi_0\rangle = 0\ , \tag{26}$$

$$P\,|\Psi^{(0)}\rangle = |\Phi_0\rangle\ , \tag{27}$$

and

$$PF_NP = PF_NQ = 0\ , \tag{28}$$

we find that the partitioned form of Eq. (10) is

$$PV_NQ\,|\Psi^{(0)}\rangle = E^{(0)}\,|\Phi_0\rangle \tag{29}$$

and

$$Q(F_N+V_N-E^{(0)})Q\,|\Psi^{(0)}\rangle=-QV_N\,|\Phi_0\rangle\ . \qquad (30)$$

From Eq. (29) it follows that the correlation energy is

$$E^{(0)}=\langle\Phi_0|\,V_NQ\,|\Psi^{(0)}\rangle\ , \qquad (31)$$

which is a formula well known from Rayleigh-Schrödinger perturbation theory. It is also well known that the solution of Eq. (30) can be written as the following expansion, where we use the resolvent $R(0)$ at $\omega=0$:

$$Q\,|\Psi^{(0)}\rangle=-\sum_{k=0}^{\infty}[R(0)(E^{(0)}-V_N)]^kR(0)V_N\,|\Phi_0\rangle\ , \qquad (32)$$

which together with the normalization condition, Eq. (17), determines $|\Psi^{(0)}\rangle$. Note also that

$$R(0)V_N\,|\Phi_0\rangle=R_2(0)V_N\,|\Phi_0\rangle\ . \qquad (33)$$

The terms in Eqs. (31) and (32) can be represented diagrammatically. We follow Paldus and Čížek[24] by letting the time flow from right to left. Resolvents may be represented by vertical lines between the interactions, but we only show them explicitly if they appear squared, i.e., a squared resolvent is designated by two vertical lines in the diagram. Furthermore, only Brandow[25] (antisymmetric) prototypes will be presented. A prototype stands for a sum of Brandow diagrams that differ from each other in that the fermion lines are oriented in distinct ways. Furthermore, all internal lines must be labeled by summation indices, see, e.g., Ref. 19 for more details.

The components

$$R_1(0)[V_N-V_NR(0)V_N-\cdots]R_2(0)V_N\,|\Phi_0\rangle \qquad (34)$$

of $|\Psi(0)\rangle$ along the singly excited states are shown in Fig. 1. Similarly the doubly excited components

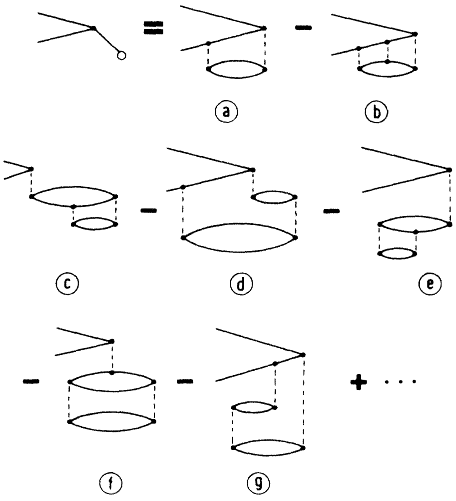

FIG. 1. Components of the CI wave function along singly excited states through third order in the correlation potential. (a)–(d) require singles and doubles in the basis, and (e)–(g) require triples also.

$$R_2(0)[-1+V_NR_2(0)-E^{(0)}R_2(0)-V_NR(0)V_NR_2(0)+\cdots]V_N\,|\Phi_0\rangle \qquad (35)$$

are shown in Fig. 2. Note that the term containing $E^{(0)}$, Fig. 2(c), is unlinked and already arises if the resolvent $R(0)$ is restricted to $R_2(0)$.

If $E^{(0)}$ is approximated by the first term of Fig. 3—which is of second order in the correlation potential V_N—the unlinked diagrams, Figs. 2(c) and 2(p), cancel each other. [Note that the two time-ordered versions of Fig. 2(p) must be included to achieve this cancellation.] It is evident that the resolvent must include at least $R_2(0)$

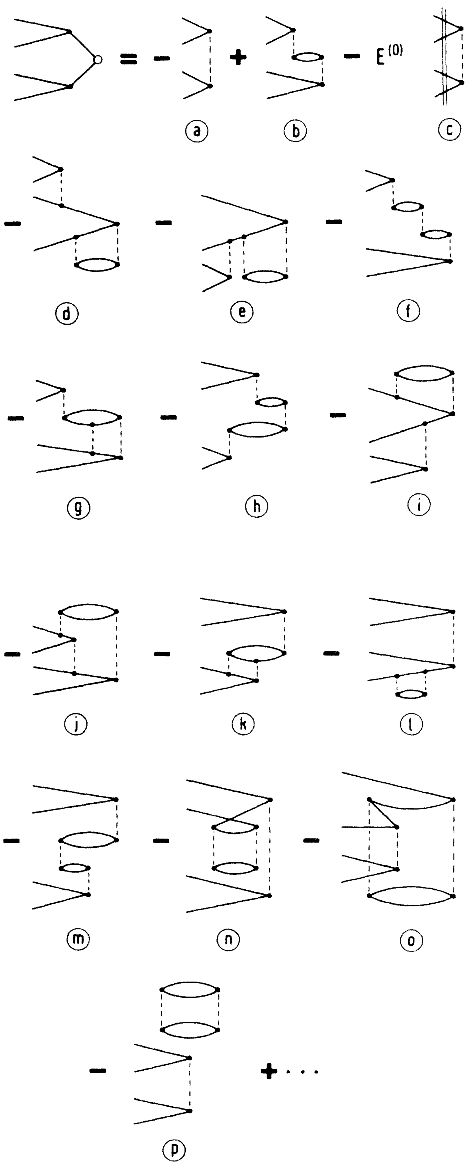

FIG. 2. Components of the CI wave function along doubly excited states through third order in the correlation potential. (a)–(h) arise in a SDCI wave function, triples are needed for (i)–(l) and quadruples for (m)–(p). The unlinked diagram (c) cancels against the two time versions of (p). The two vertical lines in (c) designate a squared resolvent.

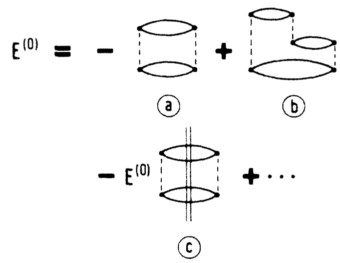

FIG. 3. Lowest-order contributions to the SDCI correlation energy. The unlinked diagram (c) can be corrected for by the Davidson-Siegbahn formula (Refs. 9 and 10), other fourth-order terms [arising from Figs. 2(d)—2(h)] are not shown.

and the four-particle term $R_4(0)$ to obtain the second unlinked term, and hence we find the well-known result that the SDCI correlation energy contains contributions from unlinked clusters. The first such cluster is of fourth order in V_N. It is easy to correct the coefficient $C^{ab}_{\alpha\beta}$ of $|\Psi^{(0)}\rangle$ along the doubly excited state $\hat{C}^{a,b}_{\alpha,\beta}|\Phi_0\rangle$, by adding the term corresponding to Fig. 2(c),

$$(C^{ab}_{\alpha\beta})_{\rm UL}=E^{(0)}\frac{\langle ab\,|\,v(1-P_{1,2})\,|\,\alpha\beta\rangle}{(\epsilon_a+\epsilon_b-\epsilon_\alpha-\epsilon_\beta)^2}\ . \tag{36}$$

Neither is it difficult to give similar expressions for resolvents expanded in Gelfand states or spin-bonded functions by the use of the hole-particle formalism described in Refs. 26 and 27, respectively.

The corresponding unlinked cluster correction to the SDCI energy [cf. Fig. 3(c)] is the well-known Davidson-Siegbahn correction.[9,10] It is perhaps of interest to point out that the Davidson-Siegbahn formula can also be obtained by coupled-cluster theory.[28]

Since in our actual calculations the zeroth-order problem is solved in a basis containing only singles and doubles, our wave function does not contain terms corresponding to Figs. 1(e)—1(g) and Figs. 2(i)—2(p). We do include, however, all terms with intermediate summations over singles and doubles to infinite order in V_N. Since, as we shall see, the solution of the first-order equation contains unlinked terms which are second order in V_N, we have not attempted to correct our zeroth-order wave function by means of Eq. (36), this being a third-order correction.

B. The first-order equation

The first-order equation, Eq. (11), can be rewritten with the aid of the reduced frequency-dependent resolvent, Eq. (21) or (23), as follows:

$$[1-R(\omega)(E^{(0)}-V_N)]\,|\,\Psi^{(1)}(\omega)\rangle = R(\omega)(\Delta E^{(1)}-W_N)\,|\,\Psi^{(0)}\rangle\ , \tag{37}$$

from which follows

$$|\,\Psi^{(1)}(\omega)\rangle = \sum_{k=0}^{\infty}[R(\omega)(E^{(0)}-V_N)]^k R(\omega)(\Delta E^{(1)}-W_N)\,|\,\Psi^{(0)}\rangle\ . \tag{38}$$

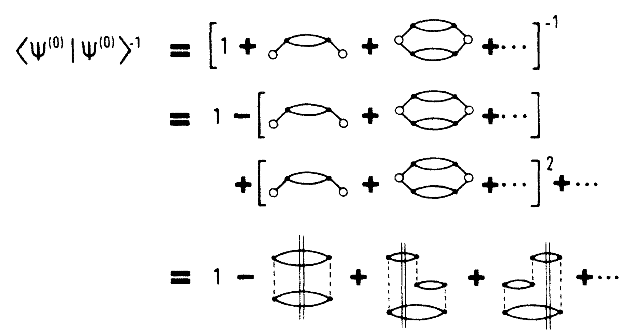

FIG. 4. Expansion of the norm of the zeroth-order wave function in orders of V_N. Cf. Eq. (17) for the intermediate normalization of $|\Psi^{(0)}\rangle$. Double vertical lines indicate squared resolvents.

The normalization factor $\langle\Psi^{(0)}|\Psi^{(0)}\rangle^{-1}$ is expanded through third order in the correlation potential in Fig. 4. The first-order energy of Fig. 5 can be combined readily with Figs. 1, 2, and 4. This reveals that the first contribution to $\Delta E^{(1)}$ is of second order in V_N (a fact which sometimes is referred to as the Møller-Plesset theorem[29]). The perturbation W being a multipolar field, $\Delta E^{(1)}$ is the correlation contribution to the permanent multipole moment of the molecule.

If we recall that $Q\,|\,\Psi^{(0)}\rangle$ starts with a first-order term and $E^{(0)}$ with a second-order term, we find that the first-order wave function is given through second order in the correlation potential V_N by

$$\begin{aligned}|\,\Psi^{(1)}(\omega)\rangle = &-R(\omega)W_N\,|\,\Psi^{(0)}\rangle\\ &-R(\omega)(E^{(0)}-V_N)R(\omega)W_N\,|\,\Psi^{(0)}\rangle\\ &-R(\omega)V_NR(\omega)V_NR(\omega)W_N\,|\,\Psi^{(0)}\rangle\ .\end{aligned} \tag{39}$$

In Fig. 6 the components are shown of the first-order wave function along the singly excited states; they are expanded up to and including terms quadratic in V_N. In Figs. 7 and 8 components along doubly and triply excited states, respectively, are given diagrammatically. In these figures only the first two terms of Eq. (39) are shown; the terms containing $E^{(0)}$, being at least of third order in V_N, are omitted.

Making the first-order approximation

$$Q\,|\,\Psi^{(0)}\rangle \approx -R_2(0)V_N\,|\,\Phi_0\rangle \tag{40}$$

[cf. Eq. (35)] and accordingly writing

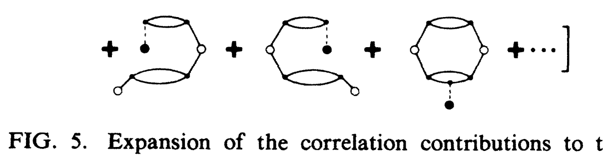

FIG. 5. Expansion of the correlation contributions to the first-order energy. The solid dot represents the interaction with the external field.

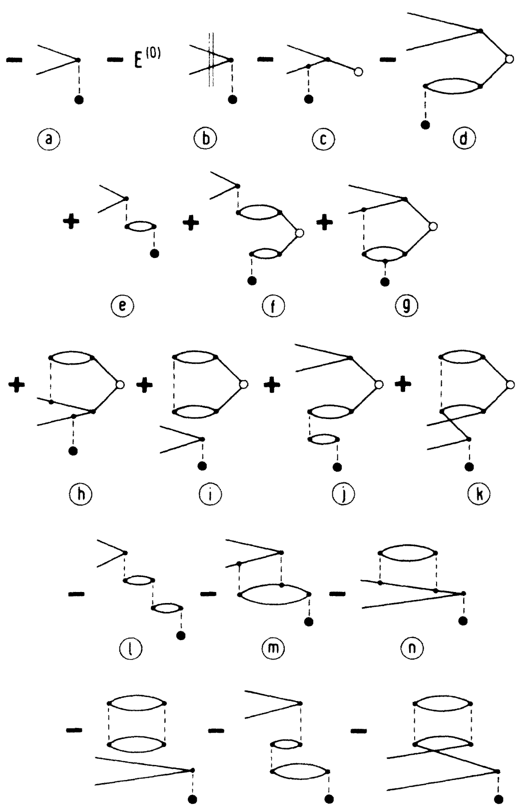

FIG. 6. Components of $\Psi^{(1)}(\omega)$ along singly excited states. The resolvents to the left of the solid dot are ω dependent. See Figs. 1 and 2 for the definition of the zeroth-order functions.

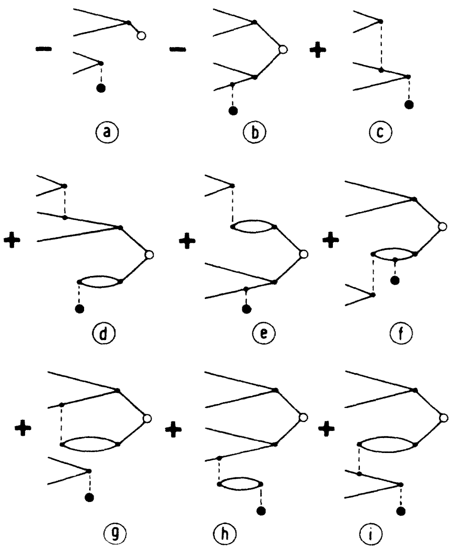

FIG. 7. Components of $\Psi^{(1)}(\omega)$ along doubly excited states. The resolvents to the left of the solid dot are ω dependent. See Figs. 1 and 2 for the definition of the zeroth-order functions.

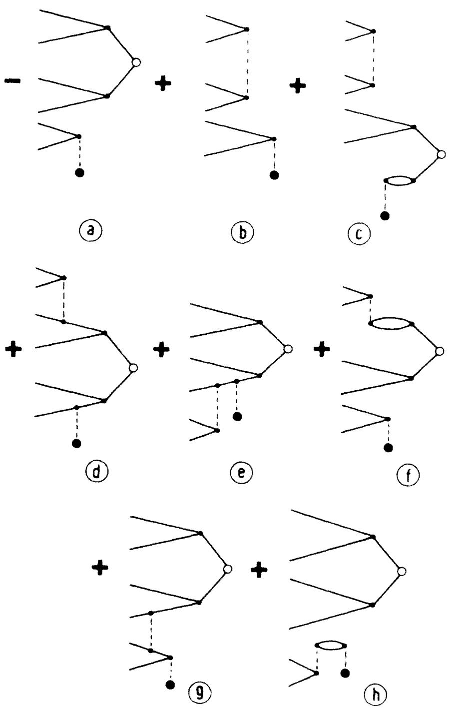

FIG. 8. Components of $\Psi^{(1)}(\omega)$ along triply excited states. The resolvents to the left of the solid dot are ω dependent. See Figs. 1 and 2 for the definition of the zeroth-order functions.

$$E^{(0)} \approx -\langle \Phi_0 | V_N R_2(0) V_N | \Phi_0 \rangle \tag{41}$$

we easily find that the three unlinked diagrams, Figs. 6(b), 6(i), and 6(o), cancel each other. Indeed, the numerators of these three diagrams are equal, and introducing the shorthand notation $\Delta_1 = \epsilon_a - \epsilon_\alpha$ and $\Delta_2 = \epsilon_a + \epsilon_b - \epsilon_\alpha - \epsilon_\beta$, we find for the denominators the rule

$$\frac{1}{\Delta_2(\Delta_1+\omega)^2} = \frac{1}{(\Delta_1+\omega)(\Delta_1+\Delta_2+\omega)\Delta_2} + \frac{1}{(\Delta_1+\omega)^2(\Delta_1+\Delta_2+\omega)} \,. \tag{42}$$

This rule is shown in Fig. 9. Hence the first-order (in W) wave function does not contain unlinked clusters of second order in V_N, but it is necessary to include the disconnected triply excited states of Fig. 8(a) in order to achieve cancellation. The algebraic expression represented by Fig. 8(a) is

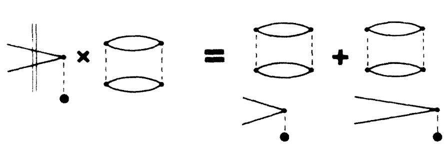

FIG. 9. Cancellation of unlinked clusters contributing to $\Psi^{(1)}(\omega)$ in second order of V_N. Cf. Eq. (44). Resolvents to the left of the solid dot are ω dependent, those to the right are for $\omega = 0$.

$$-R_3(\omega)W_N\,|\Psi^{(0)}\rangle = -\tfrac{1}{4}\sum_{\alpha,\beta,\gamma}\sum_{a,b,c} N[X_a^\dagger X_\alpha X_b^\dagger X_\beta X_c^\dagger X_\gamma]\,|\Phi_0\rangle \times \frac{\langle a\,|\,W\,|\,\alpha\rangle C^{bc}_{\beta\gamma}}{\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_\alpha-\epsilon_\beta-\epsilon_\gamma+\omega}\,, \tag{43}$$

where $C^{bc}_{\beta\gamma}$ is the coefficient of $|\Psi^{(0)}\rangle$ along $\hat{C}^{b,c}_{\beta,\gamma}\,|\Phi_0\rangle$.

It is not difficult, but tedious, to demonstrate that similar cancellations of third-order unlinked clusters occur. There are two types of such clusters: The first type arises from the third-order term in $E^{(0)}$, and the zeroth-order term (the HF component) of $\Psi^{(0)}$. In a basis containing triples cancellation will occur. The second type originates from the first-order term of $\Psi^{(0)}$ and the second-order term of $E^{(0)}$. It is easily shown that quadruply excited states are required to remove this type of unlinked clusters.

The second-order energy (the negative of the frequency-dependent polarizability), defined in Eq. (14), is shown in Fig. 10 expanded through second order in V_N. (Recall that the expansion of the components of $|\Psi^{(0)}\rangle$ along the singly excited states start in second order, and the expansion of the doubly excited components in first order.) The unlinked diagram 10(c) arises from the expansion of the normalization factor shown in Fig. 4.

Figure 10 reflects a hierarchy of approximation methods. Diagram 10(a) is the only one appearing in the UCHF (uncoupled HF) approximation, while the Tamm-Dancoff method (singly excited CI) is needed to account for 10(i) and 10(m) as well. Since we solve the first-order equation in an exact manner, we sum the Tamm-Dancoff diagrams to infinite order. The same holds for the RPA diagrams with intermediate summations over singles and doubles, which are the Tamm-Dancoff diagrams together with the other "bubble" diagrams 10(d), 10(h), and 10(j). The same diagrams appear in the (time-dependent) coupled HF method, which also sums 10(r), 10(t), and 10(x) (i.e., if we replace in Fig. 10 $\Psi^{(0)}$ by its first-order approximation). The true correlation effects[6] are accounted for by the diagrams 10(e), 10(f), 10(g), 10(k), 10(l), 10(n), 10(o), 10(u), 10(v), and 10(w).

If we expand $|\Psi^{(0)}\rangle$ through first order in V_N, we find that the numerators of the unlinked diagrams 10(b), 10(c), 10(p), 10(q), and 10(s) are equal. Using the same shorthand notation as for Eq. (44), we find for the sum D of the denominators

$$D := \frac{1}{\Delta_2(\Delta_1+\omega)^2} + \frac{1}{\Delta_2^2(\Delta_1+\omega)} - \frac{1}{\Delta_2^2(\Delta_1+\Delta_2+\omega)} - \frac{2}{(\Delta_1+\omega)(\Delta_1+\Delta_2+\omega)\Delta_2} - \frac{1}{(\Delta_1+\omega)^2(\Delta_1+\Delta_2+\omega)} = 0\,. \tag{44}$$

It is easily verified that $D=0$, which proves that the frequency-dependent polarizability does not contain unlinked clusters through second order in V_N. Since the polarizability is an extensive property (in the thermodynamic sense of the word), one expects this to hold for all orders in V_N. Indeed, this has been proved within the framework of coupled-cluster theory by Monkhorst.[30]

If we restrict the basis to singles and doubles, out of the

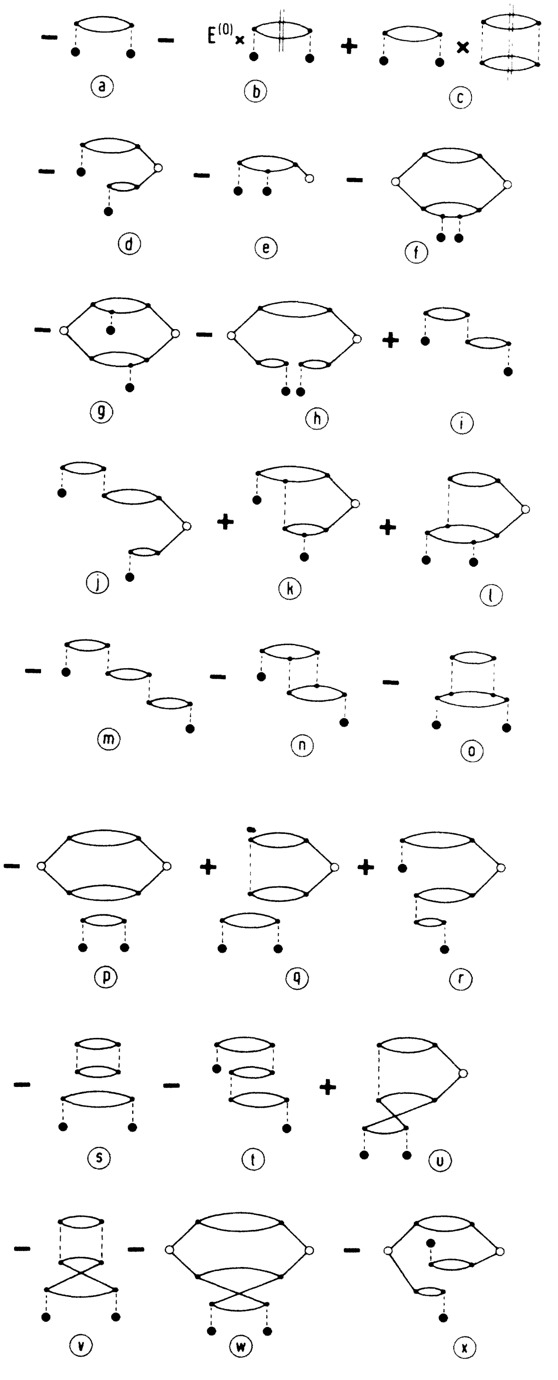

FIG. 10. Contributions to the second-order energy (the negative of the frequency-dependent polarizability) through second order in V_N. The resolvents between the solid dots are ω dependent. The mirror images of the diagrams (d), (e), (j)—(l), (q), (r), (u), and (x) are not shown but must be included. Diagrams (a)—(o) are accounted for in a basis consisting of singles and doubles, whereas (p)—(x) require triply excited states. The unlinked diagrams (b) and (c) cancel against the sum of (p), (q), and (s).

unlinked diagrams only 10(b) and 10(c) arise, and the cancellation of Eq. (46) cannot occur. In that case we can compute the contributions of these two unlinked diagrams separately, and correct the results. Algebraically diagram 10(b) is

$$E'_{\mathrm{UL}}(\omega)=E^{(0)}\sum_{\alpha,a}\frac{\langle a\,|\,W\,|\,\alpha\rangle\langle\alpha\,|\,W\,|\,a\rangle}{(\epsilon_a-\epsilon_\alpha+\omega)^2}\ . \tag{45}$$

Diagram 10(c) arises from $\langle\Psi^{(0)}\,|\,\Psi^{(0)}\rangle$. If we write C_0 for the coefficient of the HF state in the SDCI wave function—which is normalized to unity—this function can be written as $C_0\,|\,\Psi^{(0)}\rangle$, and we obtain for 10(c)

$$E''_{\mathrm{UL}}(\omega)=\alpha_{\mathrm{UCHF}}(\omega)(1-C_0^2)\ . \tag{46}$$

Note that, $E^{(0)}$ being negative, E'_{UL} is also negative and note further that E''_{UL} is positive. Since E'_{UL} appears with a minus and E''_{UL} with a plus sign in the second-order energy expression, correction for both these unlinked terms increases the polarizability.

Alternatively we can include triples in our basis. In that case we not only effectuate cancellation of the unlinked diagrams, but also obtain correlation contributions from new diagrams, such as the bubble diagrams 10(r), 10(t), and 10(x), and the true correlation diagrams 10(u), 10(v), and 10(w). It is likely that especially the EPV (exclusion principle violating) contributions of 10(u), 10(v), and 10(w) are of importance. These EPV diagrams cancel against the corresponding EPV terms of Fig. 10(q), 10(s), and 10(p), which are unlinked. Hence the cancellation of the diagrams 10(b) and 10(c) is not complete. Indeed, those terms of these latter two diagrams that are characterized by the fact that their disconnected parts have one or more summation indices in common are not unphysical and should not cancel. Although these terms do not violate the Pauli principle they are often referred to as EPV terms, the reason being that they have the same value as the sum of the EPV terms 10(u), 10(v), and 10(w). Hence, the unlinked-cluster corrections, given in Eqs. (45) and (46), overcorrect the second-order energy, and so the inclusion of triples in our CI basis will give more reliable results than the use of Eqs. (45) and (46). However, in most cases of practical interest the SDTCI basis is too large to handle, and then the SDCI values, corrected for unlinked clusters, form a good and rather reliable option.

III. COMPUTATIONAL ASPECTS

The theory of Sec. II has been tested on the neon atom. To that end we used the basis of Ref. 12, which is a $(11s,7p,2d,1f/7s,5p,2d,1f)$ basis consisting of spherical Gauss-type orbitals. The integral, self-consistent-field, and four-index transformation programs employed are all part of the ATMOL-4 set of programs.[31]

The zeroth-order problem, Eq. (10), is solved by our conventional CI program[32] in a basis of singly and doubly excited states. The lowest eigenvector and eigenvalue is obtained by Shavitt's routine,[33] which is based on the method of overrelaxation.[34]

The solution of the first-order problem, Eq. (11), has been extensively discussed in Ref. 16. Briefly, the method may be described as an *ab initio* procedure for the computation of even and odd Cauchy moments. Cauchy moments arise in the expansion of the dynamic polarizability as a power series in the frequency ω. Thus, we define the moments by the Cauchy expansion

$$\frac{\langle\Psi^{(0)}\,|\,W_N\,|\,\Psi^{(1)}(\pm\omega)\rangle}{\langle\Psi^{(0)}\,|\,\Psi^{(0)}\rangle}=\tfrac{1}{2}\sum_{k=0}^{\infty}(\pm\omega)^k S(-2-k)\ . \tag{47}$$

Recall [cf. Eq. (14)] that

$$\alpha(\omega)=-\frac{\langle\Psi^{(0)}\,|\,W_N\,|\,\Psi^{(1)}(\omega)\rangle+\langle\Psi^{(0)}\,|\,W_N\,|\,\Psi^{(1)}(-\omega)\rangle}{\langle\Psi^{(0)}\,|\,\Psi^{(0)}\rangle}\ . \tag{48}$$

With the Cauchy moments $S(-2-k)$, $k=0,1,\ldots,N$, as input, we compute the $[N,N-1]$ Padé approximant of $\alpha(\omega)$ by means of Nutall's compact formula.[35] This formula for a Padé approximant contains an inverse matrix. Rather than computing the inverse of this matrix by any of the standard methods, we diagonalize it and compute the inverse of the diagonal form. Its eigenvectors and eigenvalues constitute an "effective spectrum."[17] It can be shown[36] that this Padé approximant procedure is equivalent to the solution of the first-order equation in a Cauchy basis.[37] In practice we take N so large that the approximation to $\alpha(\omega)$ has converged, that is, an increase of N does not change the results significantly.

Once the different dynamic polarizabilities are known, the van der Waals coefficients easily follow from the Casimir-Polder[38] integral. Since the effective energies are the poles of the polarizabilities and the corresponding residues are simply the matrix elements of W_N between the effective states, the Casimir-Polder integral is most conveniently computed by the residue theorem. This gives the van der Waals coefficients their well-known form of a double sum over the spectra of the monomers, the difference with the exact formalism being that the spectra are now effective rather than exact.

In Sec. II we discussed the correlation and unlinked-cluster contributions to the second-order energy given on the left-hand side of Eq. (47). By making an expansion of this energy in powers of the frequency ω, we can apply directly the findings of Sec. II to the computation of the Cauchy moments. In particular, Eqs. (45) and (46) yield formulas for the lowest-order unlinked clusters that contaminate the Cauchy moments computed in an SDCI basis. Using the formula

$$\frac{1}{(\Delta-\omega)^2}=\sum_{k=1}^{\infty}k\frac{\omega^{k-1}}{\Delta^{k+1}}\ , \tag{49}$$

we obtain from Eq. (45)

$$E'_{\mathrm{UL}}(-\omega)=\tfrac{1}{2}E^{(0)}\sum_{k=0}^{\infty}(k+1)\omega^k S_{\mathrm{UCHF}}(-3-k)\ , \tag{50}$$

where

$$S_{\mathrm{UCHF}}(-3-k):=2\sum_{\alpha,a}\frac{\langle a\,|\,W\,|\,\alpha\rangle\langle\alpha\,|\,W\,|\,a\rangle}{(\epsilon_a-\epsilon_\alpha)^{k+2}}\ . \tag{51}$$

Hence the first unlinked-cluster correction to $S(-2-k)$ is

$$S'_{\mathrm{UL}}(-2-k)=(k+1)E^{(0)}S_{\mathrm{UCHF}}(-3-k)\ . \tag{52}$$

Recall here that $E^{(0)}$ is the SDCI correlation energy.

From Eq. (46) it follows immediately that the second unlinked-cluster correction is

$$S''_{\mathrm{UL}}(-2-k)=(1-C_0^2)S_{\mathrm{UCHF}}(-2-k)\ . \tag{53}$$

The coefficient C_0 is the component of the HF state in the SDCI wave function. The UCHF Cauchy moments defined by Eq. (51) are easy to compute; we have used the program MULTPROP (Ref. 39) to that end.

In Sec. IV we shall compare the corrected SDCI polarizabilities and van der Waals coefficients with corresponding values obtained in a CI basis augmented with triples. Unfortunately, however, the inclusion of all triply excited states is outside the scope of our CI program, so that we are forced to employ a selection procedure. In this procedure we use Eq. (43), or rather the equivalent of Eq. (43) for h-p (hole-particle) spin-bonded functions.[27]

In a basis of h-p bonded functions the three-particle resolvent, appearing on the left-hand side of Eq. (43), can be written for $\omega=0$ as

$$R_3(0)=\sum_{\{s;a,b,c;\alpha,\beta,\gamma\}}\frac{|\{s;a,b,c;\alpha,\beta,\gamma\}\rangle\langle\{s;a,b,c;\alpha,\beta,\gamma\}|}{\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_\alpha-\epsilon_\beta-\epsilon_\gamma}\ , \tag{54}$$

where the sum runs over all linearly independent triply excited bonded functions $|\{s;a,b,c;\alpha,\beta,\gamma\}\rangle$ and s, $1\leq s\leq 5$, labels the spin coupling. The selection criterion that we have applied is

$$\frac{|\langle\{s;a,b,c;\alpha,\beta,\gamma\}|W_N|\Psi^{(0)}\rangle|}{\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_\alpha-\epsilon_\beta-\epsilon_\gamma}>\delta\ . \tag{55}$$

Since the zeroth-order function $\Psi^{(0)}$ is given as an expansion of bonded functions, the computation of the numerator of Eq. (55) is reduced to the computation of a matrix element of a one-particle operator between h-p bonded functions. We have written a program for this special case of a doubly excited ket and a triply excited bra, which is based on the formulas of Ref. 27. These formulas give the matrix element the same appearance as the summand on the right-hand side of Eq. (43). The only difference is that this summand is not multiplied by a spin-symmetry coefficient as it must in a spin-adapted formalism.

To conclude we remark that we have used a "coefficient-driven" algorithm in the computation of the numerator of Eq. (55). That is, the outermost loop runs over the nonzero coefficients of $\Psi^{(0)}$, the next inner loop is over the one-electron integrals, and the innermost loop is over the spin-coupling index s. In this manner we avoid considering triples that do not interact with any doubles.

IV. RESULTS AND DISCUSSION

We have argued in Sec. II that a SDTCI basis (i.e., a basis containing all singly, doubly, and triply excited states) yields frequency-dependent polarizabilities that are correct through second-order in the correlation potential V_N. Its use should give better results than Eqs. (45) and (46), because these remove all second-order unlinked diagrams, including the EPV diagrams. Although the use of an SDTCI basis is to be preferred, we cannot handle such a large basis in full. Therefore, we have to resort to the selection procedure described in Sec. III. This selection scheme is applied for four different values of the threshold δ, defined in Eq. (55). The results are given in Table I. The dimensions listed in this table pertain to bases in which the maximum Abelian point group D_{2h} is used.

The same results are plotted in Fig. 11, where one sees clearly that the dipole polarizability α_1, the quadrupole polarizability α_2, and the van der Waals coefficients C_6 and C_8 depend linearly on δ to a very good approximation. This simple dependence enables us to extrapolate linearly these quantities to $\delta=0$. The extrapolated values are compared in Table II with results from literature.

One notices that α_1 and C_6 agree almost perfectly with the corresponding literature values, which are well established. The quantities α_2 and C_8 on the other hand, are not yet very well known. Early results are those of

TABLE I. Results for Ne and Ne_2 for different selection thresholds δ.

δ	N_1[a]	N_2[b]	α_1[c]	C_6	α_2[d]	C_8
5(−4)	2718	4689	2.609	6.310	6.728	82.36
3(−4)	4084	6730	2.627	6.359	6.764	82.90
1(−4)	8007	11729	2.647	6.408	6.803	83.45
5(−5)	10939	14794	2.654	6.424	6.820	83.66

[a] Number of triples of dipole symmetry, dimension SDCI basis: 1911.

[b] Number of triples of quadrupole symmetry, dimension of SDCI basis: 1743.

[c] α_1 is the static dipole polarizability.

[d] α_2 is the static quadrupole polarizability.

Doran,[43] who applied MBPT through second order in V_N, and used a basis of numerical HFS (Hartree-Fock-Slater) orbitals. In his work Doran included the continuum by Gauss-Laguerre quadrature over HFS continuum orbitals. Recently, Diercksen and Sadlej[42] have computed the quadrupole polarizability of the Ne atom by finite-field *SD*-MBPT (MBPT with summations over intermediate singles and doubles) through fourth order in V_N. They have used quadratically integrable orbitals (which are known to account very well for the continuum in certain cases[44]), and they have compared different basis sets. In a basis comparable to ours (their basis B) they find $\alpha_2=6.68$ a.u., which is very close to our cluster-corrected SDCI value 6.71 a.u. This seems to indicate that our approach gives results of the same quality as the finite-field *SD*-MBPT method. To test this further we applied the $(12s\,8p\,3d\,3f)$ basis D* from Ref. 42 and found $\alpha_2=7.117$ a.u. In the same basis Diercksen and Sadlej found $\alpha_2=7.48$, so that the agreement in basis B is more or less coincidental. Since the corrected SDCI values are consistently below the SDTCI static polarizabilities, it is quite possible that the value $\alpha_2=7.48$ is the better one.

It is interesting to note that the static dipole polarizability α_1 did not change by the enlargement of the basis, so that we may safely assume that the values for α_1, given in Table II, are very close to the limit of a complete orbital basis. The remaining error in the SDTCI value must be ascribed to the neglect of quadruples and perhaps relativistic effects.

The SDTCI value of C_6 coincides exactly with the semiempirical value, but the corresponding cluster-corrected value is too high. In the basis D* of Ref. 42 it is even slightly higher: 6.735 a.u. It seems that the C_6 value is not yet at the limit of a complete orbital basis, and accordingly the exact agreement between the SDTCI value and the semiempirical one is due to cancellation of errors caused by an incomplete basis and the neglect of quadruples. Note parenthetically that in earlier work from our laboratory an estimate of an SDTCI limit was given in which no excitations from the $1s$ orbital were allowed. The effect of the $1s$ excitations is not negligible, however. For instance, it increases the C_6 from 6.262 a.u. to the present value of 6.435 a.u.

TABLE II. Results for the Ne atom and the Ne_2 dimer (a.u.).

	α_1[a]	C_6	α_2[b]	C_8
TDCHF[c]	2.337	5.392	5.930	68.26
SDCI	2.324	5.587	6.026	73.20
SDCI + UL′[d]	2.591	6.345	6.624	82.45
SDCI + UL″[e]	2.651	6.688	6.706	85.54
SDTCI[f]	2.658	6.435	6.826	83.77
Literature	2.668[g]	6.43[h]	7.48[i]	73.87[j]

[a] α_1 is the static dipole polarizability.

[b] α_2 is the static quadrupole polarizability.

[c] Reference 12.

[d] First unlinked-cluster correction, cf. Eq. (45).

[e] First and second unlinked-cluster corrections, cf. Eqs. (45) and (46).

[f] Extrapolated to zero selection threshold.

[g] Semiempirical estimate, Ref. 40.

[h] Semiempirical estimate, Ref. 41.

[i] MBPT calculations, Ref. 42.

[j] MBPT calculations, Ref. 43.

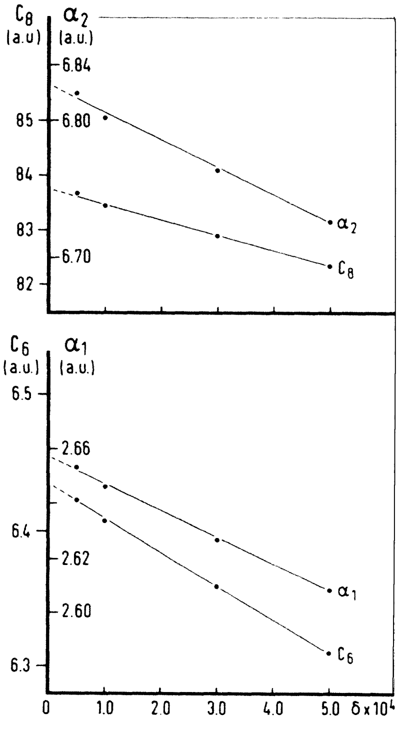

FIG. 11. Dipole polarizability α_1, quadrupole polarizability α_2, and the dispersion coefficients C_6 and C_8 as functions of the triples selection threshold δ, cf. Eq. (57).

Our SDTCI value of C_8 is considerably larger than Doran's value,[43] but the same is true for α_2, and since our α_2 value is probably too small, it is fair to assume that our C_8 value is better than Doran's. Furthermore, our experience so far indicates that upon enlargement of the orbital basis the SDTCI value always increases, so that the value $C_8=83.77$ is likely to be too low. This is confirmed by our calculations in the basis D* of Ref. 42, which give a cluster-corrected C_8 value of 90.59, which is 5.5% higher than the corresponding value in the smaller basis. If we assume that the SDTCI value is too low by a similar percentage, we arrive at an estimate for the exact value: $C_8\approx88$ a.u.

The TDCHF values given in Table II were obtained in the same atomic-orbital basis as is used in the present work. We can therefore give a rather accurate estimate of the true correlation effects. They are 12.1%, 16.2%, 13.1%, and 18.5% for α_1, C_6, α_2, and C_8, respectively.

From the theory in Sec. II it follows that the two unlinked-cluster corrections given in Eqs. (45) and (46) must bring the SDCI results close to the full SDTCI results. It is therefore of interest to compare the cluster-corrected SDCI values with those obtained in an SDTCI basis, irrespective of the fact whether these latter quantities are the most accurate available. From the figures in Table II we find that α_1 and α_2 are, respectively, 0.3% and 1.8% below the corresponding SDTCI reference

TABLE III. Effective dipole and quadrupole SDTCI spectrum of the Ne atom.

Dipole		Quadrupole	
T_0^1	E	T_0^2	E
0.509 134	0.730 710	0.976 405	0.747 281
0.929 985	1.155 466	−1.758 727	1.597 128
−0.793 889	3.067 341	0.687 742	2.650 636
0.344 377	5.908 007	0.361 427	5.879 463

values. The corresponding errors in the SDCI basis being 12.6% and 11.7%, respectively, we see that the improvement by the unlinked-cluster formulas is large. Stated differently, this means that the main reason for the poor behavior of a SDCI treatment based on unperturbed orbitals is the contamination of the second-order energy by unlinked clusters. The contributions of the unlinked diagrams have about the same absolute value as those of the true correlation diagrams, but are of opposite sign.

The fact that the static cluster-corrected polarizabilities are below the SDTCI polarizabilities must probably be ascribed to the diagrams in Figs. 10(t)–10(x), which contribute to the latter, but not to the former.

The corrected C_6 and C_8 values are, respectively, 3.9% and 1.8% above the SDTCI reference values. The improvement over the uncorrected SDCI van der Waals coefficients is considerable, since these are about 12% too low.

Another possible way of extrapolating the results obtained in truncated SDTCI bases is by linearly extrapolating the Cauchy moments to $\delta=0$. The advantage of this is that the extrapolated Cauchy moments yield an extrapolated effective spectrum, which is essentially of full SDTCI quality. This effective spectrum is given in Table III. This spectrum reproduces the fifth line of Table II to four-figure accuracy, if we use the formulas

$$\alpha_l(\omega)=\sum_{i=1}^{n}(T_0^l)_i^2\left[\frac{1}{E_i-\omega}+\frac{1}{E_i+\omega}\right] \tag{56}$$

and

$$C_{2l_a+2l_b+2}=(2-\delta_{l_a,l_b})\frac{(2l_a+2l_b)!}{(2l_a)!(2l_b)!}\times\sum_{i,j=1}^{n}\frac{(T_0^{l_a})_i^2(T_0^{l_b})_j^2}{E_i^a+E_j^b}\,, \tag{57}$$

where $(T_0^l)_i$ and E_i are listed in Table III for $i=1,2,3,4$.

V. SUMMARY AND CONCLUSIONS

The most important result of this paper is that (frequency-dependent) SDCI polarizabilities are in error by about 12%, when the CSF's (configuration state functions) in which the first-order wave function is expanded are constructed from unperturbed orbitals. These errors are caused by the contamination of the first-order wave function and the second-order energy with unlinked clusters. Unfortunately, it is at present not feasible to perturb the orbitals in *time-dependent* fields to at least second order, which would be required for a reliable calculation of time-dependent second-order properties.

We have shown that there are two different ways to improve upon the SDCI results obtained in an unrelaxed orbital basis:

(i) by inclusion of triply excited CSF's in the CI basis,

(ii) by the correction formulas given in Eqs. (45) and (46) of this paper.

The first method gives rise to very large CI basis sets, but is in principle a better method than the second. The second method has the advantage of being cheap and easy to apply and also improves the SDCI results considerably, as can be seen in Table II. It gives polarizabilities and van der Waals coefficients of the Ne atom and the Ne_2 dimer which deviate less than 4% from those obtained in the SDTCI basis.

ACKNOWLEDGMENTS

The authors wish to thank Dr. B. Jeziorski for his careful reading of the manuscript and for his useful comments.

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