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### Dynamic Multipole Polarizabilities of Two- and Four-Electron Atomic Systems\*

G. P. Arrighini

*Istituto di Chimica Fisica dell'Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy*

F. Biondi

*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56100 Pisa, Italy*

C. Guidotti

*Laboratorio di Chimica Quantistica ed Energetica Molecolare del Consiglio Nazionale delle Ricerche, Via Risorgimento 35, 56100 Pisa, Italy*

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Dynamic multipole polarizabilities of a number of simple atomic closed-shell systems in their ground states have been calculated within the coupled time-dependent Hartree-Fock scheme. The systems here investigated include He, Li<sup>+</sup>, Be<sup>2+</sup>, B<sup>3+</sup>, C<sup>4+</sup>, Be, B<sup>+</sup>, and C<sup>2+</sup>. In order to acquire some feeling about the obtained results, the dipole polarizabilities have been evaluated either by using a scalar- or a vector-potential representation for the oscillating external field: these two choices give rise to the well-known polarizability expressions in terms of "length" and "velocity" oscillator strengths, respectively. Furthermore, a unitary transformation of the Hartree-Fock Hamiltonian is devised, which allows one to use a perturbation operator corresponding to that involved in the "acceleration" oscillator-strength expression. Estimates of transition energies to low-lying excited states have been also obtained from the frequency values at which the various polarizabilities display discontinuities.

#### I. INTRODUCTION

At present there is a keen interest for a deeper and wider knowledge of the response of atomic and molecular systems to external electric and magnetic fields.

Besides the long awareness that the basis for understanding optical properties of atoms and molecules is provided by the quantum theory of the interaction between electromagnetic fields and matter, a major stimulus for such an interest has been given by the recognition that long-range dispersion energy coefficients between atoms and/or molecules are obtainable, through the Casimir-Polder formula,<sup>1-4</sup> after analytic extension of polarizability data to imaginary arguments. (For a different, equivalent, approach to this problem, see Ref. 5.) In this regard, refractive index measurements appear to be valuable sources of information at infrared, visible, and near-ultra-

violet frequencies, but their extension to shorter wavelengths is thus far hindered by vacuum-ultra-violet technique difficulties. Even though some clever methods based on powerful mathematical tools, such as Padé approximants,<sup>6</sup> theory of moments,<sup>7-9</sup> linear programming,<sup>8,10</sup> etc., have been devised for an optimal utilization of the available data, it seems manifest that only the isotropic lowest long-range expansion coefficient (that corresponding to the rotationally averaged dipole-dipole interaction) can be accurately obtained in this way, unless dynamic multipole polarizabilities higher than the dipole one become measurable. In this regard, it is to be remarked that the knowledge of higher interaction coefficients is more and more required, in view of the increased effort to provide fairly sophisticated intermolecular potential functions (see, for instance, Ref. 11) and because experiments seem to be ripe for revealing the effect of higher than  $R^{-6}$  terms.<sup>12</sup> More-

over, if anisotropic contributions to the dispersion energy are desired,<sup>13</sup> a knowledge of the principal components of the polarizability tensor (or, equivalently, its anisotropies) as a function of frequency is required; it appears very hard to reach this knowledge even in the simplest case (dipole-dipole contribution). Thus, reliable estimates or, possibly, accurate and detailed predictions have still to rely, in general, upon theoretical *ab initio* calculations.

At the same time, moderate size many-electron systems acted upon by weak time-dependent external fields have been shown to be tractable by either effective perturbative or variational-perturbative techniques (for a good review, see Ref. 14), founded on the Hartree-Fock (HF) scheme. Since the linear response of atoms and molecules to external fields is individuated once the proper first-order perturbation equation has been solved, the reliability of obtained results hopefully depends, to the largest extent, on how well solutions to such equation may be approximated. This appears to be particularly true if the coupled HF scheme<sup>14,15</sup> is employed, because it is known that such an approximation is correct to first order in the residual potential and contains, moreover, additional correction terms to all orders in the same potential (a rather detailed "diagrammatic" proof can be found in Ref. 15).

This paper is concerned with the evaluation of various dynamic multipole polarizabilities of simple two- and four- electron closed-shell atoms and ions in their ground states, i.e., He, Li<sup>+</sup>, Be<sup>2+</sup>, B<sup>3+</sup>, C<sup>4+</sup>, Be, B<sup>+</sup>, and C<sup>2+</sup>, using the time-dependent HF scheme. No attempts are here made to utilize such quantities for the prevision of long-range interaction coefficients; this task will eventually be undertaken in a future paper. Some emphasis will be placed on the degree of invariance of the results under some kinds of unitary transformations of the HF Hamiltonian, such as to generate perturbation operators which, in the dipole case, are represented by  $\vec{r}$  ("length"),  $\vec{v}$  ("velocity"), and  $\vec{v}U$  ("acceleration"), respectively. Moreover, some discussion about transition energies to low-lying excited states (which here appear as the frequencies at which polarizabilities become infinite) will be attempted.

## II. THEORY

It is known that the time-dependent HF approximation can be formulated by a density-matrix approach.<sup>16-18</sup> Since the theory involved has been recently reviewed in some detail,<sup>19</sup> we shall limit ourselves here to a sketchy presentation of the main formulas for the case of a spherically sym-

metric system acted on by an external, inhomogeneous, oscillating electric field  $\vec{\mathcal{E}}(\vec{r}, t)$ . If the field is assumed to be very weak, the equation of motion for the Dirac density operator  $\rho(t)$ ,  $[H(\rho), \rho] = i\partial\rho/\partial t$ , can be linearized, by putting  $\rho(t) = \rho_0 + \delta\rho(t)$ , to give

$$[H(\rho_0), \delta\rho] + [H(\delta\rho), \rho_0] = i \frac{\partial}{\partial t} (\delta\rho) \quad (1)$$

[atomic units (a.u.) will be used throughout]. The unperturbed stationary Dirac density operator associated to the ground state of the system satisfies the time-independent equation

$$[H(\rho_0), \rho_0] = 0, \quad (2)$$

$H(\rho_0)$  and  $H(\delta\rho)$  being the unperturbed and the first-order perturbed Hamiltonian operators, respectively. If  $|n\rangle$  denotes a generic one-particle eigenstate (spin-orbital) of  $H(\rho_0)$  with energy  $\epsilon_n$ , the representative  $\langle n | \delta\rho | n' \rangle$  of  $\delta\rho$  is seen to satisfy the equation

$$\left[ i \frac{\partial}{\partial t} - (\epsilon_n - \epsilon_{n'}) \right] \langle n | \delta\rho | n' \rangle = (f_{n'} - f_n) \langle n | H(\delta\rho) | n' \rangle. \quad (3)$$

In deriving Eq. (3) we have used the standard representation for  $\rho_0$ ,  $\rho_0 = \sum_n f_n |n\rangle \langle n|$ ,  $f_n$  being the distribution function (equal to unity if  $|n\rangle$  is an occupied state; zero otherwise).

If  $W(t)$  denotes the interaction term between external field  $\vec{\mathcal{E}}(\vec{r}, t)$  and electrons, it can be shown<sup>17,19</sup> that

$$\langle n | H(\delta\rho) | n' \rangle = \langle n | W(t) | n' \rangle + \sum_{m, m'} \langle n m' | n' m \rangle_{AS} \langle m | \delta\rho | m' \rangle, \quad (4)$$

where  $\langle n m' | n' m \rangle_{AS} = \langle n m' | n' m \rangle - \langle n m' | m n' \rangle$ .

Now  $\vec{\mathcal{E}}(\vec{r}, t)$  can be represented by a scalar potential  $\Phi$ , i.e.,  $\vec{\mathcal{E}}(\vec{r}, t) = -\vec{\nabla}\Phi$ ; choosing

$$\Phi(\vec{r}, t) = -\frac{1}{2}(e^{i\omega t} + e^{-i\omega t}) \sum_{l=1}^{\infty} A_l \left( \frac{4\pi}{2l+1} \right)^{1/2} r^l Y_l^0(\theta, \varphi), \quad (5)$$

it is easily seen that the  $z$  component of the oscillating inhomogeneous electric field results:

$$\mathcal{E}_z(\vec{r}, t) = \frac{1}{2}(e^{i\omega t} + e^{-i\omega t}) \times \sum_{l=0}^{\infty} A_l \left( \frac{4\pi}{2l+1} \right)^{1/2} (l+1)r^l Y_l^0(\theta, \varphi),$$

so that  $A_1, A_2, \dots$  are proportional to the values of the  $z$  component of electric field, gradient of electric field  $z$ -component, ..., respectively, at  $\vec{r} = 0$ ,  $t = 0$ . Therefore

$$\begin{aligned} \langle n|W(t)|n' \rangle &= -\langle n|\Phi|n' \rangle \\ &= \sum_{l=1}^{\infty} \left( \frac{4\pi}{2l+1} \right)^{1/2} A_l(t) \langle n|r^l Y_l^0(\theta, \varphi)|n' \rangle \end{aligned}$$

having put  $A_l(t) = \frac{1}{2} A_l (e^{i\omega t} + e^{-i\omega t})$ . The form of the perturbation term suggests the following ansatz for  $\delta\rho$ <sup>17,20</sup>:

$$\delta\rho^{(\omega)}(t) = \sum_l A_l [e^{i\omega t} \delta\rho_l^{(\omega)+} + e^{-i\omega t} \delta\rho_l^{(\omega)-}],$$

which defines the new time-independent (but frequency-dependent) operators  $\delta\rho_l^{(\omega)\pm}$ . (For the meaning of the superscript  $L$ , see below.) The equations for the unknown operators  $\delta\rho_l^{(\omega)\pm}$  are easily obtained:

$$\begin{aligned} [(\epsilon_n - \epsilon_{n'}) \pm \omega] \langle n|\delta\rho_l^{(\omega)\pm}|n' \rangle \\ = (f_n - f_{n'}) \left[ \frac{1}{2} \left( \frac{4\pi}{2l+1} \right)^{1/2} \langle n|r^l Y_l^0|n' \rangle \right. \\ \left. + \sum_{mm'} \langle nm'|n'm \rangle_{AS} \langle m|\delta\rho_l^{(\omega)\pm}|m' \rangle \right]. \quad (6) \end{aligned}$$

The (linear) induced electric multipole moment  $\langle \mu_l \rangle$  is given by

$$\langle \mu_l \rangle = \text{Tr} [\mu_l \delta\rho^{(\omega)}],$$

where

$$\mu_l = - \left( \frac{4\pi}{2l+1} \right)^{1/2} r^l Y_l^0(\theta, \varphi)$$

is the operator associated with the  $l$ th multipole moment. The  $2^l$ -pole dynamic polarizability at the frequency  $\omega$  is defined as

$$\alpha_l^{(\omega)} = \frac{\partial \langle \mu_l \rangle}{\partial A_l(t)} = \text{Tr} [\mu_l (\delta\rho_l^{(\omega)+} + \delta\rho_l^{(\omega)-})]. \quad (7)$$

Owing to the form of the perturbation operator involved, Eq. (7) will be referred to as "length" expression of the polarizability. The superscript  $L$  was used just to emphasize it.

As an alternative, the electric field  $\vec{\mathcal{E}}(\vec{r}, t)$  could be introduced into the Hamiltonian by means of a vector potential  $\vec{A}$ , through  $\vec{\mathcal{E}}(\vec{r}, t) = -(1/c)\partial\vec{A}/\partial t$ . Since this change of description corresponds to a gauge transformation  $(\Phi, 0) \rightarrow (0, \vec{A})$ , with  $\vec{A} = \vec{\nabla}\chi$ ,  $0 = \Phi - (1/c)\partial\chi/\partial t$ ,  $\chi$  being the gauge function, invariance of physically observable properties under such a kind of transformation would be a desirable feature of any theory, even though approximate. The coupled HF theory—either time independent<sup>21</sup> or time dependent<sup>22</sup>—actually has this pleasant attribute; we think it of some interest to explicitly show such an invariance, even though the result is already known,<sup>22</sup> because the procedure will later permit us to attain the "acceler-

ation" expression of the dynamic polarizabilities within the HF scheme.

The transformed density operator  $\tilde{\rho} = e^{(i/c)S(t)} \times \rho e^{-i(c)S(t)}$  is easily seen to satisfy the motion equation  $[\tilde{H} - (1/c)\partial S/\partial t, \tilde{\rho}] = i\partial\tilde{\rho}/\partial t$ ,  $\tilde{H}$  being the transformed HF Hamiltonian. Assuming the Hermitian operator  $S(t)$  to be of the same order of smallness as  $H(\delta\rho)$ , the new equation of motion, after linearization, becomes

$$[H(\rho_0), \delta\tilde{\rho}] + [H(\delta\tilde{\rho}) - (1/c)\frac{\partial S}{\partial t}, \rho_0] = i\frac{\partial}{\partial t}(\delta\tilde{\rho}), \quad (8)$$

where  $H(\delta\tilde{\rho}) = H(\delta\rho) + (i/c)[S, H(\rho_0)]$ ; hence the  $\langle n|\delta\tilde{\rho}|m \rangle$  representative of  $\delta\tilde{\rho}$  satisfies the equation

$$\begin{aligned} [(\epsilon_n - \epsilon_m) - i\frac{\partial}{\partial t}] \langle n|\delta\tilde{\rho}|m \rangle = (f_n - f_m) \langle n|H(\delta\rho) \\ - \frac{i}{c} [H(\rho_0), S] - \frac{1}{c} \frac{\partial S}{\partial t} |m \rangle. \quad (9) \end{aligned}$$

If  $S(t)$  is restricted to be an operator diagonal in the coordinate representation, Eq. (8) can be transformed into the new one (see Appendix A)

$$\begin{aligned} [(\epsilon_n - \epsilon_m) - i\frac{\partial}{\partial t}] \langle n|\delta\tilde{\rho}|m \rangle \\ = (f_n - f_m) \left\{ \langle n|W - \frac{1}{c}\frac{\partial S}{\partial t} + \frac{i}{2c}(\nabla^2 S) + \frac{i}{c}\vec{\nabla}S \cdot \vec{\nabla}|m \rangle \right. \\ \left. + \sum_{pq} \langle p|\delta\tilde{\rho}|q \rangle \langle nq|mp \rangle_{AS} \right\}, \quad (10) \end{aligned}$$

which only involves  $\delta\tilde{\rho}$ . By choosing now  $S$  in such a way that  $W - (1/c)\partial S/\partial t = 0$ , i.e.,

$$\begin{aligned} S(\vec{r}, t) = (c/2i\omega)(e^{i\omega t} - e^{-i\omega t}) \\ \times \sum_{l=1}^{\infty} \left( \frac{4\pi}{2l+1} \right)^{1/2} r^l Y_l^0(\theta, \varphi), \end{aligned}$$

and noting that  $\nabla^2 S = 0$ , the interaction term on the right-hand side in Eq. (10),  $(i/c)\langle n|\vec{\nabla}S \cdot \vec{\nabla}|m \rangle$ , takes the same form one would obtain directly starting with a description in terms of a vector potential ( $\chi = -S$ ). Moreover, from  $\langle \mu_l \rangle = \text{Tr}(\mu_l \delta\rho^{(\omega)})$  and Eq. (A3), it follows that

$$\begin{aligned} \langle \mu_l \rangle &= \text{Tr}(\mu_l \delta\rho^{(V)}) - \frac{i}{c} \text{Tr}(\mu_l [S, \rho_0]) \\ &= \text{Tr}(\mu_l \delta\rho^{(V)}), \end{aligned}$$

from which the equality between  $\alpha_l^{(\omega)}$  and  $\alpha_l^{(V)}$  directly arises. (The superscript  $V$  has been introduced to mean velocity.)

The "acceleration" expression for  $\alpha_l(\omega)$  within the HF scheme will be derived only for the case  $l = 1$  (dipole polarizability) and to attain it a Schwinger-type unitary transformation<sup>23,24</sup> is the

proper one. The starting point is the equation of motion for  $\rho^{(A)}$ ; if we let  $\rho^{(A)} = e^{(i/c)T(t)}\rho^{(V)}e^{-(i/c)T(t)}$  (the superscript  $A$  stands for acceleration), at first order

$$\delta\rho^{(A)} = \delta\rho^{(V)} + \frac{i}{c} [T(t), \rho_0].$$

Therefore, from Eq. (6)

$$[H(\rho_0), \delta\rho^{(A)}] - \frac{i}{c} [[H(\rho_0), T], \rho_0] + [H(\delta\rho^{(V)}), \rho_0] + \frac{i}{c} \frac{\partial}{\partial t} [T, \rho_0] = i \frac{\partial}{\partial t} (\delta\rho^{(A)}). \quad (11)$$

If we let  $T(t) = -(c/\omega^2)A_1(t)p_x$  [so that  $(1/c)T(t) = -(1/\omega^2)A_1(t)p_x$  is the generator of a translation along  $z$  of the amount  $A_1(t)/\omega^2$ , the classical displacement of a particle of unit charge and mass due to the electric field  $A_1(t)$ ], Eq. (11) for the  $\langle n | \delta\rho^{(A)} | m \rangle$  representative becomes

$$\begin{aligned} & \left[ (\epsilon_n - \epsilon_m) - i \frac{\partial}{\partial t} \right] \langle n | \delta\rho^{(A)} | m \rangle \\ &= (f_n - f_m) \left\{ \frac{i}{c} \langle n | [T, H(\rho_0)] | m \rangle + \sum_{p \neq q} \langle nq | mp \rangle_{AS} \right. \\ & \quad \left. \times \left( \langle p | \delta\rho^{(A)} | q \rangle + \frac{i}{c} \langle p | [\rho_0, T] | q \rangle \right) \right\}. \end{aligned} \quad (12)$$

From the identity (see Appendix B)

$$\begin{aligned} & \sum_{p \neq q} \langle nq | mp \rangle_{AS} \langle p | [T, \rho_0] | q \rangle - \langle n | [T, H(\rho_0)] | m \rangle \\ &= (c/\omega^2)A_1(t) \langle n | [p_x, U] | m \rangle, \end{aligned} \quad (13)$$

where  $U$  is the nuclear attraction potential energy operator, Eq. (12) can be recast in the final form, only involving  $\delta\rho^{(A)}$ ,

$$\alpha_i(\omega) = 4 \sum_M^{\text{occ}} \sum_{M'}^{\text{unocc}} \langle N | \delta\rho_i^+ + \delta\rho_i^- | N' \rangle \langle N' | \mu_i | N \rangle, \quad (15)$$

$$\begin{aligned} & (\epsilon_N - \epsilon_{N'}) \langle N | \delta\rho_i^+ + \delta\rho_i^- | N' \rangle + \omega \langle N | \delta\rho_i^+ - \delta\rho_i^- | N' \rangle \\ &= \langle N | \mu_i | N' \rangle + \sum_M^{\text{occ}} \sum_{M'}^{\text{unocc}} [4 \langle NM' | N'M \rangle - \langle NM' | MN' \rangle - \langle NM | M'N' \rangle] \langle M | \delta\rho_i^+ + \delta\rho_i^- | M' \rangle \\ & \quad \times (\epsilon_N - \epsilon_{N'}) \langle N | \delta\rho_i^+ - \delta\rho_i^- | N' \rangle + \omega \langle N | \delta\rho_i^+ + \delta\rho_i^- | N' \rangle \\ &= \sum_M^{\text{occ}} \sum_{M'}^{\text{unocc}} [\langle NM | M'N' \rangle - \langle NM' | MN' \rangle] \langle M | \delta\rho_i^+ - \delta\rho_i^- | M' \rangle. \end{aligned} \quad (16)$$

In the two summations above, capital unprimed (primed) letters denote, respectively, occupied (unoccupied) orbitals (assumed to be real).

For each  $\omega$  value, the inhomogeneous system (16) can be solved for the unknown quantities

$$\begin{aligned} & \left[ (\epsilon_n - \epsilon_m) - i \frac{\partial}{\partial t} \right] \langle n | \delta\rho^{(A)} | m \rangle \\ &= (f_n - f_m) \left[ -\frac{1}{\omega^2} A_1(t) \langle n | \frac{\partial U}{\partial z} | m \rangle \right. \\ & \quad \left. + \sum_{p \neq q} \langle nq | mp \rangle_{AS} \langle p | \delta\rho^{(A)} | q \rangle \right], \end{aligned}$$

since, in the coordinate representation,  $p_x = -i \partial / \partial z$ . For an atomic system of nuclear charge  $Z$ ,  $\partial U / \partial z = Zz/r^3$ , so that the well-known expression for the perturbation in the "acceleration" version<sup>25</sup> results.

Unlike "length" and "velocity" expressions of the induced moments, which are form invariant, the "acceleration" expression is not such; it is easily verified that in the latter case

$$\begin{aligned} \langle \mu_i \rangle &= \text{Tr}(\mu_i \delta\rho^{(A)}) - \frac{i}{c} \text{Tr}(\mu_i [T, \rho_0]) \\ &= \text{Tr}(\mu_i \delta\rho^{(A)}) - \frac{\mathfrak{K}}{\omega^2} A_1(t), \end{aligned}$$

$\mathfrak{K}$  being the number of electrons. Therefore

$$\alpha_i^{(A)}(\omega) = \text{Tr}[\mu_i (\delta\rho^{(A)+} + \delta\rho^{(A)-})] - \frac{\mathfrak{K}}{\omega^2} \quad (14)$$

is the proper expression of the dipole polarizability in the "acceleration" version.

### III. COMPUTATIONAL SCHEME AND RESULTS

Equation (6) or the equivalent equations for  $\langle n | \delta\rho^{(V)\pm} | m \rangle$  and  $\langle n | \delta\rho^{(A)\pm} | m \rangle$  is not yet in a suitable form for actual computations. As a first convenient step we pass from spin-orbitals to orbitals, summing with respect to the spin quantum numbers<sup>19</sup>; then we get equations for the representatives of  $(\delta\rho_i^+ + \delta\rho_i^-)$ ,  $(\delta\rho_i^+ - \delta\rho_i^-)$ :

$\langle N | \delta\rho_i^+ \pm \delta\rho_i^- | N' \rangle$  by standard techniques, for instance iteratively. In this regard, however, our experience has been rather negative, because of lack of convergence as the frequency  $\omega$  gets closer and closer to the "resonances" of the atom,

although some proposed expedients<sup>26</sup> to avoid such troubles were exploited. For this reason we have preferred to apply to noniterative methods of solution. If we introduce the column supervectors  $\delta\rho_i^+ + \delta\rho_i^- \equiv \underline{U}_h^{(i)}$ ,  $\delta\rho_i^+ - \delta\rho_i^- \equiv \underline{U}_a^{(i)}$  and  $\underline{\mu}_i$ , and the supermatrices

$$\begin{aligned}\underline{V}_{NN', MM'} &= 2\langle NM' | N'M \rangle - \langle NM' | MN' \rangle, \\ \underline{V}'_{NN', MM'} &= 2\langle NM' | N'M \rangle - \langle NM | M'N' \rangle, \\ \underline{\epsilon}_{NN', MM'}^{\text{TD}} &= (\epsilon_{N'} - \epsilon_N) \delta_{NM} \delta_{N'M'} + \underline{V}_{NN', MM'},\end{aligned}\quad (17)$$

Eqs. (15) and (16) can be written in matrix form as follows:

$$\begin{aligned}\alpha_i(\omega) &= 4\underline{\mu}^{(i)\dagger} \underline{U}_h^{(i)}, \\ (\underline{\epsilon}^{\text{TD}} + \underline{V}') \underline{U}_h^{(i)} - \omega \underline{U}_a^{(i)} &= \underline{\mu}^{(i)}, \\ (\underline{\epsilon}^{\text{TD}} - \underline{V}') \underline{U}_a^{(i)} - \omega \underline{U}_h^{(i)} &= 0.\end{aligned}\quad (18)$$

The equation system (19) can formally be solved for  $\underline{U}_h^{(i)}$ , so to give

$$\alpha_i(\omega) = 4\underline{\mu}^{(i)\dagger} [(\underline{\epsilon}^{\text{TD}} + \underline{V}') - \omega^2(\underline{\epsilon}^{\text{TD}} - \underline{V}')^{-1}]^{-1} \underline{\mu}^{(i)}.\quad (20)$$

All three matrices  $\underline{\epsilon}^{\text{TD}}$ ,  $\underline{V}$ , and  $\underline{V}'$  are symmetric with respect to the simultaneous exchange ( $N \rightleftharpoons M$ ), ( $N' \rightleftharpoons M'$ ).  $\underline{\epsilon}^{\text{TD}}$  is recognizable as the matrix to be diagonalized in the so-called Tamm-Dancoff approximation<sup>27,28</sup> for singlet excited states. The matrix  $\underline{V}'$  involves elements corresponding to double excitations, so that it is usually claimed to introduce electron correlation effects.<sup>18,28,29</sup>

From the identity

$$\begin{aligned}[(\underline{\epsilon}^{\text{TD}} + \underline{V}') - \omega^2(\underline{\epsilon}^{\text{TD}} - \underline{V}')^{-1}]^{-1} \\ = [(\underline{\epsilon}^{\text{TD}} - \underline{V}')(\underline{\epsilon}^{\text{TD}} + \underline{V}') - \omega^2 \underline{1}]^{-1}(\underline{\epsilon}^{\text{TD}} - \underline{V}')\end{aligned}\quad (21)$$

the polarizability  $\alpha_i(\omega)$  can be cast into the form<sup>19</sup>

$$\begin{aligned}\alpha_i(\omega) &= 4\underline{\mu}^{(i)\dagger} [(\underline{\epsilon}^{\text{TD}} - \underline{V}')(\underline{\epsilon}^{\text{TD}} + \underline{V}') - \omega^2 \underline{1}]^{-1} \\ &\times (\underline{\epsilon}^{\text{TD}} - \underline{V}') \underline{\mu}^{(i)},\end{aligned}\quad (22)$$

which makes very clear that  $\alpha_i(\omega)$  has poles whenever the square frequency  $\omega^2$  of the external field equals any eigenvalues of the *non-Hermitian* matrix  $(\underline{\epsilon}^{\text{TD}} - \underline{V}')(\underline{\epsilon}^{\text{TD}} + \underline{V}')$ .

A second, *fully equivalent*, expression for  $\alpha_i(\omega)$ , namely,

$$\begin{aligned}\alpha_i(\omega) &= 4\underline{\mu}^{(i)\dagger}(\underline{\epsilon}^{\text{TD}} - \underline{V}') \\ &\times [(\underline{\epsilon}^{\text{TD}} + \underline{V}')(\underline{\epsilon}^{\text{TD}} - \underline{V}') - \omega^2 \underline{1}]^{-1} \underline{\mu}^{(i)}\end{aligned}\quad (22')$$

is obtained by means of a second identity analogous to (21). Now the poles will occur in correspondence with any eigenvalues of the different *non-Hermitian* matrix  $(\underline{\epsilon}^{\text{TD}} + \underline{V}')(\underline{\epsilon}^{\text{TD}} - \underline{V}')$ , the adjoint of that previously found. On the other hand, Eqs. (22) and (22') are two fully equivalent expressions for  $\alpha(\omega)$  at any  $\omega$  value, so that it appears physically sound to require the following eigenvalue equations to be simultaneously satisfied:

$$(\underline{\epsilon}^{\text{TD}} - \underline{V}')(\underline{\epsilon}^{\text{TD}} + \underline{V}') \underline{C}_{NN'} = \underline{C}_{NN'} \Omega_{NN'}^2, \quad (23)$$

$$(\underline{\epsilon}^{\text{TD}} + \underline{V}')(\underline{\epsilon}^{\text{TD}} - \underline{V}') \underline{D}_{NN'} = \underline{D}_{NN'} \Omega_{NN'}^2 \quad (23')$$

for the same eigenvalues  $\Omega_{NN'}^2$  and different eigenvectors  $\underline{C}_{NN'}$ ,  $\underline{D}_{NN'}$ . It can be pointed out that Eq. (23) is only another form of the random-phase approximation (RPA) secular problem, which follows from the more conventional one<sup>28,30</sup> by simple algebraic manipulations.<sup>31</sup> Having recovered this result is completely to be expected, since the equivalence between RPA and (linearized) time-dependent HF (TDHF) schemes is a well-established point<sup>15,18,32-34</sup> and our present treatment of the TDHF approximation in the density-matrix context is fully equivalent to other approaches.<sup>15,18,33-35</sup>

If  $\underline{D}$  denotes the matrix whose columns are the eigenvectors  $\underline{D}_{NN'}$  of Eq. (23'), Eq. (22') can be recast in the form

$$\alpha_i(\omega) = 4\underline{\mu}^{(i)\dagger}(\underline{\epsilon}^{\text{TD}} - \underline{V}') \underline{D} [\underline{\Omega}^2 - \omega^2 \underline{1}]^{-1} \underline{D}^{-1} \underline{\mu}^{(i)}, \quad (24)$$

which substantially reduces the evaluation of  $\alpha_i(\omega)$  to solve the eigenvalue problem (23') taking into account the orthonormality requirement  $\underline{D}_{MM'}^\dagger \underline{C}_{NN'} = \delta_{NM} \delta_{N'M'}$  which stems from Eqs. (23) and (23'). The procedure we have followed is that described by Ullah and Rowe,<sup>36</sup> which under sufficiently mild conditions succeeds to reduce the original problem to one for a symmetric matrix of half the dimensions.

If the (diagonal) matrix  $[\underline{\Omega}^2 - \omega^2 \underline{1}]^{-1}$  is expanded about  $\omega = 0$ , the polarizability expression, Eq. (24), can be cast in the Cauchy form<sup>37,38</sup>

$$\alpha_i(\omega) = \sum_{k=0}^{\infty} \omega^{2k} \xi_k^{(i)}, \quad (25)$$

the Cauchy moment  $\xi_k^{(i)}$  being given by

$$\xi_k^{(i)} = 4\underline{\mu}^{(i)\dagger}(\underline{\epsilon}^{\text{TD}} - \underline{V}') \underline{D} \underline{\Omega}^{-2(k+1)} \underline{D}^{-1} \underline{\mu}^{(i)}. \quad (26)$$

As can be immediately seen,  $\xi_0^{(i)}$  represents the 2<sup>l</sup>-pole *static* polarizability.

Expressions analogous to (24) and (26) can be obtained, of course, in the "velocity" and "acceleration" versions.

For all systems investigated in this paper but He atom, the occupied HF single-particle states

$\langle \tilde{r} | N, L = 0, M = 0 \rangle$  have been approximated by Clementi's analytic representations in terms of Slater-type orbitals, using in any case the largest available basis set.<sup>39</sup> For the He atom, we chose a four Slater-type orbital representation ("compromise SCF function" in Ref. 40). The departure of this function from the "best SCF function"<sup>40</sup> has been analyzed by us over a range of 10 a.u., the largest difference resulting 0.0005 at the nucleus, to become 0.00001 at a distance of 1.5 a.u. Even the unoccupied HF orbitals  $\langle \tilde{r} | N', L = l, 0 \rangle$  have been represented in terms of a basis of Slater-type functions<sup>5,41,42</sup> of proper symmetry by merely orthogonalizing and diagonalizing them with respect to the HF Hamiltonian since they cannot contribute to the ground-state wave function for symmetry reasons. In this regard, we point out that the radial part of the latter orbitals is a finite linear combination of the form  $\sum_{j,k} A_{jk} r^{n_j-1} e^{-\zeta'_k r}$ . Extension of the basis set as well as values for the quantum numbers  $n'_j$  and orbital exponents  $\zeta'_j$  are completely arbitrary and interconnected; in any case they should be chosen in such a way as to represent as well as possible the distortion induced by the external field in the charge-density distribution. As a result of empirical tests we have found that once fixed a  $n'_j$  value, orbital exponents  $\zeta'_k$  of importance are approximately located around the values  $\zeta' = [(2n' + 1)/2(n + l) + 1] \zeta$  which maximize the transition multipole moment matrix elements  $\langle n0\xi | \mu_l | n'l\xi' \rangle$ . This is not unexpected, since an unperturbed orbital  $|N, L = 0, M = 0\rangle$  transforms approximately in  $\mu_l |N, L = 0, M = 0\rangle$  owing to the presence of the external perturbation, and "excited" states of importance to represent it seem to be those which largely overlap with  $\mu_l |N, L = 0, M = 0\rangle$ . Such a choice for the orbital exponents leads to reject as rather unimportant very low  $\zeta'$  values which, in principle, could appear relevant, for they heavily contribute to generate low-lying unoccupied states. On the other hand, one is faced also by the necessity of avoiding too large overlap matrix elements  $\langle n'_j l \zeta'_k | n'_k l \zeta'_m \rangle$  which cause troubles in the orthonormalization procedure associated with the determination of the unoccupied orbitals,<sup>5</sup> so that some compromise between the above requirements is very often the due toll. In each case the procedure was tested by enlarging the basis set of orbitals of proper symmetry. To the aim of appreciating the convergence behavior in a typical case, in Table I some dipole polarizability values of  $\text{Li}^+$  are reported at a few frequencies as the extension of the basis set was enlarged. The convergence is seen to be quite good and the agreement with the values obtained for instance by Kaveeshwar *et al.*<sup>43</sup> is excellent [even these authors employed TDHF

theory in its coupled form; their starting point was the Frenkel's variational principle<sup>16</sup> with trial functions of the generalized Hássé type  $Y_i^0(\theta) \sum_s C_{is} r^{n_{is}} e^{-\zeta_{is} r}$ . No other convergence test will be reported in order not to cumber excessively this paper; we limit ourselves to the assertion that in any case a rather smooth convergence was found.

In Tables II and III, apart from a few exceptions, the first five Cauchy moments for the various multipole polarizabilities of He and Be isoelectronic sequences are presented, along with the range of frequencies  $\Delta\omega$  over which they allow to reproduce calculated values of polarizabilities with a maximum error of about 0.5%. Values of comparison from other calculations are also reported. All of these have been obtained by coupled TDHF theory in its variational formulation,<sup>16,35,43</sup> with trial functions of the generalized Hássé type. The only quoted experimental Cauchy moments (dipole polarizability of He) have been obtained by constrained least-squares fitting of refractive index data.<sup>37</sup> The values for He labeled DV have been obtained by identifying the proper coefficients in the  $\omega^2$  expansion of

$$\alpha_l(\omega) = \sum_{i=1}^5 a_{li} / (\omega_{li}^2 - \omega^2)$$

given by Dalgarno and Victor<sup>44</sup> which should provide, along with those by Kaveeshwar *et al.* (KCH),<sup>43</sup> rather accurate comparison terms; the values labeled MSM have been analogously obtained from the simpler interpolating formula  $\alpha(\omega) = A/(1 - B\omega^2)$  used by Mukherjee *et al.*<sup>45</sup> From the inspection of these tables the agreement between our values and other calculations appears to be satisfying; the relatively larger discrepancies which are manifest in the case of quadrupole and octopole Cauchy moments of He are at present a

TABLE I. Check of convergence for the dipole polarizability  $\alpha_1(\omega)$  of  $\text{Li}^+$ .  $N$  is the employed number of Slater-type functions  $n_p(\xi)$  of  $p$  symmetry.

$\omega$ (a.u.)	$N = 2^a$	$N = 6^b$	$N = 8^c$	KCH <sup>d</sup>
0.00	0.1823	0.1895	0.1895	0.1895
0.25	0.1835	0.1911	0.1911	0.1911
0.50	0.1876	0.1963	0.1963	0.1963
1.00	0.2053	0.2206	0.2207	0.2207

<sup>a</sup>  $\{2p(2.4516); 2p(4.3894)\}$ .

<sup>b</sup> As footnote (a) +  $\{2p(6.0385); 3p(3.4322); 3p(6.1452); 3p(8.4539)\}$ .

<sup>c</sup> As footnote (b) +  $\{2p(1.2651); 3p(1.7711)\}$ .

<sup>d</sup> See Ref. 43.

bit puzzling, and could indicate an imperfect convergence of our procedure in these cases. As a general comment, however, it seems one may confirm that using virtual orbitals of HF type as a tool for representing the distortion caused by time-dependent external fields is a valuable alternative to the more used procedure in terms of generalized Hassé type functions. This remark could be of some value in connection with more complex systems, especially molecules.

Approximate correlations between  $\xi_0^{(l)}$  values (i.e.,  $2^l$ -pole static polarizabilities) and nuclear charge  $Z$  are expressed by

$$\begin{aligned}
 (\text{He sequence}): \quad & \xi_0^{(1)} = 29.32Z^{-4.5}, \\
 & \xi_0^{(2)} = 342.3Z^{-7.2}, \quad \xi_0^{(3)} = 6919Z^{-9.6}; \\
 (\text{Be sequence}): \quad & \xi_0^{(1)} = 9.64 \times 10^4 Z^{-5.6}, \\
 & \xi_0^{(2)} = 2.14 \times 10^8 Z^{-9.8}, \quad \xi_0^{(3)} = 6.79 \times 10^{12} Z^{-13.6}.
 \end{aligned} \tag{27}$$

TABLE II. Cauchy moments (a.u.) for the He isoelectronic sequence.

		$\xi_0^{(1)}$	$\xi_1^{(1)}$	$\xi_2^{(1)}$	$\xi_3^{(1)}$	$\xi_4^{(1)}$	$\Delta\omega^a$	
He	$l=1$	This paper <sup>b</sup>	0.1318(+01) <sup>c</sup>	0.1375(+01)	0.1708(+01)	0.2313(+01)	0.3236(+01)	0 ÷ 0.5
		KCH <sup>d</sup>	0.1322(+01)	0.1388(+01)	0.1735(+01)	0.2358(+01)		
		LK <sup>e</sup>	0.1322(+01)	0.1386(+01)	0.1730(+01)	0.2350(+01)	0.3346(+01)	
		DV <sup>f</sup>	0.1322(+01)	0.1386(+01)	0.1729(+01)	0.2348(+01)	0.3345(+01)	
		MSM <sup>g</sup>	0.1293(+01)	0.1435(+01)	0.1593(+01)	0.1768(+01)	0.1963(+01)	
		Expt. <sup>h</sup>	0.1384(+01)	0.1550(+01)	0.2066(+01)	0.295 (+01)		
He	$l=2$	This paper	0.2286(+01)	0.1650(+01)	0.1445(+01)	0.1415(+01)	0.1491(+01)	0 ÷ 0.6
		DV <sup>f</sup>	0.2326(+01)	0.1704(+01)	0.1512(+01)	0.1499(+01)	0.1602(+01)	
	$l=3$	This paper	0.9542(+01)	0.5578(+01)	0.3951(+01)	0.3165(+01)	0.2760(+01)	0 ÷ 0.6
	$l=3$	DV <sup>f</sup>	1.0095(+01)	0.6025(+01)	0.4396(+01)	0.3654(+01)	0.3362(+01)	
	$l=4$	This paper	0.7310(+02)	0.3721(+02)	0.2274(+02)	0.1582(+02)	0.1207(+02)	0 ÷ 0.7
Li <sup>+</sup>	$l=1$	This paper <sup>b</sup>	0.1895(+00)	0.2624(-01)	0.4172(-02)	0.7086(-03)	0.1247(-03)	0 ÷ 1.5
		KCH <sup>d</sup>	0.1895(+00)	0.2635(-01)	0.418 (-02)	0.713 (-03)		
		MSM <sup>g</sup>	0.1870(+00)	0.2749(-01)	0.4041(-02)	0.5940(-03)	0.0873(-03)	
	$l=2$	This paper	0.1121(+00)	0.0100(+00)	0.1066(-02)	0.1246(-03)	0.155 (-04)	0 ÷ 1.7
	$l=3$	This paper	0.1662(+00)	0.1191(-01)	0.1016(-02)	0.0966(-03)	0.99 (-05)	0 ÷ 1.8
Be <sup>2+</sup>	$l=1$	This paper <sup>b</sup>	0.5186(-01)	0.1906(-02)	0.7927(-04)	0.3494(-05)	0.1589(-06)	0 ÷ 2.5
		KCH <sup>d</sup>	0.5187(-01)	0.1834(-02)	0.7688(-04)			
		MSM <sup>g</sup>	0.5139(-01)	0.1994(-02)	0.7736(-04)	0.3002(-05)	0.1165(-06)	
	$l=2$	This paper	0.153 (-01)	0.353 (-03)	0.95 (-05)	0.3 (-06)		0 ÷ 3
	$l=3$	This paper	0.116 (-01)	0.213 (-03)	0.46 (-05)	0.1 (-06)		0 ÷ 3
B	$l=1$	This paper <sup>b</sup>	0.1959(-01)	0.2667(-03)	0.4076(-05)	0.6574(-07)	0.1091(-08)	0 ÷ 5
		MSM <sup>g</sup>	0.1942(-01)	0.2758(-03)	0.3943(-05)	0.5639(-07)	0.0806(-08)	
	$l=2$	This paper	0.3426(-02)	0.2859(-04)	0.2786(-06)	0.2966(-08)	0.3339(-10)	0 ÷ 6.5
	$l=3$	This paper	0.1543(-02)	0.101 (-04)	0.1 (-06)			0 ÷ 5
C <sup>4+</sup>	$l=1$	This paper <sup>b</sup>	0.8938(-02)	0.5497(-04)	0.3780(-06)	0.2737(-08)	0.2037(-10)	0 ÷ 7
		MSM <sup>g</sup>	0.8879(-02)	0.5825(-04)	0.3821(-06)	0.2507(-08)	0.1644(-10)	
	$l=2$	This paper	0.1046(-02)	0.38 (-05)				0 ÷ 4
	$l=3$	This paper	0.309 (-03)	0.9 (-06)				0 ÷ 5

<sup>a</sup>  $\Delta\omega$  is the frequency range (a.u.) over which the tabulated Cauchy moments allow to reproduce calculated polarizability values with a maximum error of 0.5%.

<sup>b</sup> These Cauchy moments correspond to polarizabilities evaluated in the "length" version.

<sup>c</sup> 0.1318(+01) = 1.318.

<sup>d</sup> See Ref. 43.

<sup>e</sup> See Ref. 6.

<sup>f</sup> See Ref. 44.

<sup>g</sup> See Ref. 45.

<sup>h</sup> See text and Ref. 37.

TABLE III. Cauchy moments (a.u.) for the Be isoelectronic sequence.

		$\xi_0^{(l)}$	$\xi_1^{(l)}$	$\xi_2^{(l)}$	$\xi_3^{(l)}$	$\xi_4^{(l)}$	$\Delta\omega^a$	
Be	$l=1$	This paper <sup>b</sup>	0.4562(+02)	0.1434(+04)	0.4591(+05)	0.1474(+07)	0.4736(+08)	0÷0.1
		KCH <sup>c</sup>	0.4562(+02)	0.1427(+04)	0.4508(+05)	0.1427(+07)		
		E <sup>d</sup>	0.4486(+02)	0.1354(+04)	0.1664(+05)	0.3103(+07)		
	$l=2$	This paper	0.3426(+03)	0.4095(+04)	0.5346(+05)	0.7357(+06)	0.1047(+10)	0÷0.15
		$l=3$ This paper	0.5624(+04)	0.4714(+05)	0.4441(+06)	0.4512(+07)	0.4828(+08)	0÷0.1
		$l=4$ This paper	0.1641(+06)	0.1114(+07)	0.8558(+07)	0.7164(+08)	0.6383(+09)	0÷0.2
B <sup>+</sup>	$l=1$	This paper <sup>b</sup>	0.1140(+02)	0.1150(+03)	0.1214(+04)	0.1288(+05)	0.1369(+06)	0÷0.15
		KCH <sup>c</sup>	0.1139(+02)	0.1132(+03)	0.1180(+04)	0.1238(+05)		
	$l=2$ This paper	0.2868(+02)	0.5886(+02)	0.1270(+03)	0.2821(+03)	0.6372(+03)	0÷0.25	
$l=3$ This paper	0.1851(+03)	0.2423(+03)	0.3455(+03)	0.5243(+03)	0.8317(+03)	0÷0.25		
C <sup>2+</sup>	$l=1$	This paper <sup>b</sup>	0.4512(+01)	0.2323(+02)	0.1279(+03)	0.7092(+03)	0.3934(+04)	0÷0.25
		KCH <sup>c</sup>	0.4506(+01)	0.2299(+02)	0.1253(+03)	0.6885(+03)		
	$l=2$ This paper	0.5250(+01)	0.3348(+01)	0.2211(+01)	0.1489(+01)	0.1016(+01)	0÷0.7	
$l=3$ This paper	0.1799(+02)	0.7019(+01)	0.2939(+01)	0.1287(+01)	0.5797(+00)	0÷0.8		

<sup>a</sup> See footnote (a) of Table II.<sup>b</sup> See footnote (b) of Table II.<sup>c</sup> See Ref. 43.<sup>d</sup> See Ref. 42.

The exponent  $-4.5$  for  $\xi_0^{(1)}$  in the He isoelectronic series is very close to that found by Natori *et al.*<sup>46</sup> ( $-4.4$ ); some extrapolations by means of Eqs. (27) up to  $Z = 10$  ( $\text{Ne}^{8+}$ ) provided reasonably accurate estimates for  $\alpha_1(0)$  when compared with values by Tuan *et al.*<sup>47</sup> and Cohen<sup>48</sup> [the largest discrepancy ( $\text{Ne}^{8+}$ ) is about 10%]. It may be pointed out that the coefficient 29.32 a.u., which should be interpreted as dipole polarizability of  $\text{H}^-$ , is actually

very far from the coupled HF estimate.<sup>49</sup>

In order to appreciate in some quantitative way the degree of completeness of the basis sets used in this paper, a number of dipole Cauchy moments obtained in the three versions "length," "velocity," and "acceleration" are presented in Table IV, together with two other quantities of related interest,  $\xi_{-1}^{(A)}$  and  $\sum_{NN'} f_{NN'}^{(L)}$ . If Eq. (14) is manipulated along lines similar to the development leading to

TABLE IV. Comparison of some dipole Cauchy moments in the "length" ( $L$ ), "velocity" ( $V$ ), and "acceleration" ( $A$ ) versions.

		$\xi_0$	$\xi_1$	$\xi_2$	$\xi_3$	$\xi_4$	$\xi_{-1}^{(A)}$	$\sum_{NN'} f_{NN'}^{(L)}$
He	$L$	0.1318(+01)	0.1375(+01)	0.1708(+01)	0.2313(+01)	0.3286(+01)		1.9998
	$V$	0.1320(+01)	0.1381(+01)	0.1719(+01)	0.2331(+01)	0.3314(+01)		
	$A$	0.1319(+01)	0.1380(+01)	0.1721(+01)	0.2336(+01)	0.3323(+01)	1.9995	
Li <sup>+</sup>	$L$	0.1895(+00)	0.2624(-01)	0.4172(-02)	0.7086(-03)	0.1247(-03)		1.9999
	$V$	0.1895(+00)	0.2624(-01)	0.4171(-02)	0.7083(-03)	0.1247(-03)		
	$A$	0.1893(+00)	0.2624(-01)	0.4178(-02)	0.7096(-03)	0.1248(-03)	1.9998	
Be <sup>2+</sup>	$L$	0.5186(-01)	0.1906(-02)	0.7927(-04)	0.3494(-05)	0.1589(-06)		2.0044
	$V$	0.5109(-01)	0.1899(-02)	0.7903(-04)	0.3482(-05)	0.1583(-06)		
	$A$	0.5184(-01)	0.1902(-02)	0.7904(-04)	0.3482(-05)	0.1583(-06)	1.9961	
Be	$L$	0.4562(+02)	0.1434(+04)	0.4591(+05)	0.1474(+07)	0.4736(+08)		4.0004
	$V$	0.4559(+02)	0.1433(+04)	0.4588(+05)	0.1473(+07)	0.4733(+08)		
	$A$	0.4509(+02)	0.1413(+04)	0.4548(+05)	0.1461(+07)	0.4697(+08)	3.9923	



Eqs. (24)–(26), the result

$$\begin{aligned}\alpha_1^{(A)}(\omega) &= \frac{1}{\omega^2} \{4\mu^{(1)\dagger}(\underline{\epsilon}^{\text{TD}} - \underline{V}') \\ &\quad \times \underline{D}[\underline{\Omega}^2 - \omega^2 \underline{1}]^{-1} \underline{D}^{-1}(\underline{\nabla} \underline{U}) - \mathfrak{N}\} \\ &= \frac{1}{\omega^2} \{ \xi_{-1}^{(A)} + \omega^2 \xi_0^{(A)} + \omega^4 \xi_1^{(A)} + \dots - \mathfrak{N} \}\end{aligned}$$

is found,  $(\underline{\nabla} \underline{U})$  being the (column) supervector of components  $(\underline{\nabla} \underline{U})_{NN'} = Z(z/r^3)_{NN'}$ . Thus it is clear that

$$\xi_{-1}^{(A)} = 4\mu^{(1)\dagger}(\underline{\epsilon}^{\text{TD}} - \underline{V}') \underline{D} \underline{\Omega}^{-2} \underline{D}^{-1}(\underline{\nabla} \underline{U})$$

must equal the number of electrons  $\mathfrak{N}$  [Kuhn - Thomas sum rule in the "acceleration" version] in order that  $\alpha_1^{(A)}(\omega)$  approaches a finite limit ( $\xi_0^{(A)}$ ) as  $\omega \rightarrow 0$ .<sup>50</sup>  $\sum_{NN'} f_{NN'}^{(L)}$  is the analogous sum rule in the length version. It can be shown that

the sum rule  $\xi_{-1}^{(A)} = \mathfrak{N}$  is verified if the basis set of expansion includes  $z|N\rangle$  and  $p_x|N\rangle$  for each occupied single-particle state  $|N\rangle$ , while in order that  $\sum_{NN'} f_{NN'}^{(L)} = \mathfrak{N}$  it is sufficient that the basis set contain  $z|N\rangle$  for all occupied  $|N\rangle$ 's.<sup>51</sup> Moreover, this second condition is sufficient for the equality  $\xi_k^{(L)} = \xi_k^{(V)}$ ,  $\forall k$ . The departures of  $\sum_{NN'} f_{NN'}^{(L)}$  and  $\xi_{-1}^{(A)}$  from  $\mathfrak{N}$  are therefore a measure of how much our basis sets are capable to represent  $z|N\rangle$  and  $p_x|N\rangle$  in the form  $\sum_\gamma |\gamma\rangle\langle\gamma|z|N\rangle$  or  $\sum_\gamma |\gamma\rangle\langle\gamma|p_x|N\rangle$ , i.e., how much the projection operator  $\sum_\gamma |\gamma\rangle\langle\gamma|$  is close to the identity and, of course, the requirement  $\xi_{-1}^{(A)} = \mathfrak{N}$  is more severe than  $\sum_{NN'} f_{NN'}^{(L)} = \mathfrak{N}$ . The inspection of the values for Be makes clear that the discrepancies  $\xi_k^{(A)} - \xi_k^{(L)} \approx \xi_k^{(A)} - \xi_k^{(V)}$  are mainly imputable to an imperfect representation of  $p_x|2s\rangle$ , so that some improvement could be carried out along this line.

TABLE V. Transition frequencies (a.u.) from dynamic polarizability calculations for He sequence.

	Transition	This paper	MSM <sup>a</sup>	MMS <sup>b</sup>	KCH <sup>c</sup>	Expt. <sup>d</sup>
He	$1s^2 \rightarrow 1s2p$	0.7969	0.797		0.7966	0.7798
	$1s^2 \rightarrow 1s3p$	0.8636	0.863			0.8485
	$1s^2 \rightarrow 1s4p$	0.8877	0.887			0.8726
	$1s^2 \rightarrow 1s5p$	0.9041	0.898			0.8838
	$1s^2 \rightarrow 1s3d$	0.8624		0.8624		0.8480
	$1s^2 \rightarrow 1s4d$	0.8867		0.8867		0.8724
	$1s^2 \rightarrow 1s5d$	0.9007		0.8979		0.8837
	$1s^2 \rightarrow 1s4f$	0.9024		0.8867		0.8724
	$1s^2 \rightarrow 1s5f$	0.9998		0.8979		0.8837
	$1s^2 \rightarrow 1s5g$	0.9082				
Li <sup>+</sup>	$1s^2 \rightarrow 1s2p$	2.3051	2.304			2.2866
	$1s^2 \rightarrow 1s3p$	2.6724	2.573			2.5597
	$1s^2 \rightarrow 1s3d$	2.5830		2.5702		2.5576
	$1s^2 \rightarrow 1s4d$	2.8776		2.6674		2.6549
	$1s^2 \rightarrow 1s4f$	2.7118		2.6673		2.6549
Be <sup>2+</sup>	$1s^2 \rightarrow 1s2p$	4.5641	4.562			4.5451
	$1s^2 \rightarrow 1s3p$	5.3749	5.172			5.1596
	$1s^2 \rightarrow 1s3d$	5.1675		5.1671		
	$1s^2 \rightarrow 1s4d$	5.3859		5.3857		
	$1s^2 \rightarrow 1s4f$	5.4704		5.3856		
B <sup>3+</sup>	$1s^2 \rightarrow 1s2p$	7.5729	7.572			7.5549
	$1s^2 \rightarrow 1s3p$	8.6609	8.661			8.6492
	$1s^2 \rightarrow 1s3d$	8.6548		8.6532		
	$1s^2 \rightarrow 1s4d$	9.1916		9.0419		
	$1s^2 \rightarrow 1s4f$	9.1880		9.0417		
C <sup>4+</sup>	$1s^2 \rightarrow 1s2p$	11.3336	11.331			11.3150
	$1s^2 \rightarrow 1s3p$	13.4691	13.038			13.0288
	$1s^2 \rightarrow 1s3d$	13.0846				
	$1s^2 \rightarrow 1s4d$	14.6827				
	$1s^2 \rightarrow 1s4f$	13.8602				

<sup>a</sup> See Ref. 45.

<sup>b</sup> See Ref. 51.

<sup>c</sup> See Ref. 43.

<sup>d</sup> See C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stds. Circ. No. 467 (U. S. GPO, Washington, D. C., 1949).

TABLE VI. Transition frequencies (a.u.) from dynamic polarizability calculations for Be sequence.

	Transition	This paper	KCH <sup>a</sup>	AG <sup>b</sup>	Expt. <sup>c</sup>
Be	$2s^2 \rightarrow 2s2p$	0.1764	0.1758	0.188	0.1940
	$2s^2 \rightarrow 2s3p$	0.2490		0.266	0.2742
	$2s^2 \rightarrow 2s4p$	0.3211		0.292	0.3063
	$2s^2 \rightarrow 2s5p$	0.4881		0.311	
	$2s^2 \rightarrow 2s3d$	0.2548			0.2936
	$2s^2 \rightarrow 2s4d$	0.3003			0.3134
	$2s^2 \rightarrow 2s5d$	0.3998			0.3235
	$2s^2 \rightarrow 2s4f$	0.2856			
	$2s^2 \rightarrow 2s5f$	0.3430			
	$2s^2 \rightarrow 2s5g$	0.2943			
B <sup>+</sup>	$2s^2 \rightarrow 2s2p$	0.3068			0.3344
	$2s^2 \rightarrow 2s3p$	0.6228			0.6566
	$2s^2 \rightarrow 2s3d$	0.6583			0.7048
	$2s^2 \rightarrow 2s4d$	0.8920			0.7999
	$2s^2 \rightarrow 2s4f$	0.7489			0.7970
C <sup>2+</sup>	$2s^2 \rightarrow 2s2p$	0.4246			0.4664
	$2s^2 \rightarrow 2s3p$	1.1420			1.1798
	$2s^2 \rightarrow 2s3d$	1.1977			1.2598
	$2s^2 \rightarrow 2s4d$	1.4134			1.4773
	$2s^2 \rightarrow 2s4f$	1.4151			1.4704

<sup>a</sup> See Ref. 43.

<sup>b</sup> See Ref. 29.

<sup>c</sup> See footnote (d) in Table V.

Tables V and VI contain transition frequencies for He and Be isoelectronic sequences, respectively, along with comparison terms. The values there reported are, of course, the same obtainable in the random-phase approximation<sup>15,19,28-30</sup> in terms of the employed basis sets. For the He

sequence, besides experimental values, we have selected several values from Mukherjee *et al.*<sup>45</sup> ( $1s^2 \rightarrow 1snp$ ) and from the very extensive (and accurate) tables in the paper by Moitra *et al.*<sup>52</sup> (column labeled MMS) ( $1s^2 \rightarrow 1snd$ ,  $1s^2 \rightarrow 1snf$ ). As far as the Be sequence is concerned, we are aware only of a few estimates for the Be atom (columns labeled KCH, AG). The RPA calculations by Altick and Glassgold (AG) compare fairly well with experience, even though more approximate orbitals of Hartree-type were employed as a basis set. It may be observed that, unlike the He sequence, the calculated frequencies are generally smaller than the experimental ones. This finding was ascertained by performing calculations of the same frequencies also in the Tamm-Dancoff approximation<sup>19,27,28</sup>: In this new scheme the computed values already resulted lower than the observed ones. Since it is known<sup>19,53</sup> that  $\Omega^{\text{TD}} \geq \Omega^{\text{RPA}}$ , one has to conclude that the various singly excited states of the Be sequence are affected by the lack of electronic correlation at a smaller extent than the corresponding ground states.

We propose to investigate the problem of foreseeing both transition frequencies and oscillator strengths, in the various approximations, in a future paper.

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#### APPENDIX A

For any operator  $S$  which is diagonal in the coordinate representation, it can be verified that

$$\langle n | [H(\rho_0), S] | m \rangle = -\langle n | \frac{1}{2}(\nabla^2 S) + \vec{\nabla} S \cdot \vec{\nabla} | m \rangle + \sum_p f_p \langle np | \frac{S(\vec{r}) - S(\vec{r}')}{|\vec{r} - \vec{r}'|} | pm \rangle; \quad (\text{A1})$$

from Eqs. (4) and (A1), Eq. (7) transforms as follows:

$$\left[ (\epsilon_n - \epsilon_m) - i \frac{\partial}{\partial t} \right] \langle n | \delta \bar{\rho} | m \rangle = (f_n - f_m) \left\{ \langle n | W - \frac{1}{c} \frac{\partial S}{\partial t} + \frac{i}{2c} (\nabla^2 S) + \frac{i}{c} \vec{\nabla} S \cdot \vec{\nabla} | m \rangle + \sum_q \langle p | \delta \rho | q \rangle \langle nq | m p \rangle_{AS} - \frac{i}{c} \sum_p f_p \langle np | \frac{S(\vec{r}) - S(\vec{r}')}{|\vec{r} - \vec{r}'|} | pm \rangle \right\}. \quad (\text{A2})$$

From

$$\langle p | \delta \rho | q \rangle = \langle p | \delta \bar{\rho} | q \rangle - \frac{i}{c} \langle p | [S, \rho_0] | q \rangle = \langle p | \delta \bar{\rho} | q \rangle - \frac{i}{c} (f_p - f_q) \langle p | S | q \rangle, \quad (\text{A3})$$

after using the completeness property of the single-particle states  $|q\rangle$ , we finally get, from (A2), the linearized equation

$$\left[ (\epsilon_n - \epsilon_m) - i \frac{\partial}{\partial t} \right] \langle n | \delta \bar{\rho} | m \rangle = (f_n - f_m) \left\{ \langle n | W - \frac{1}{c} \frac{\partial S}{\partial t} + \frac{i}{2c} (\nabla^2 S) + \frac{i}{c} \vec{\nabla} S \cdot \vec{\nabla} | m \rangle + \sum_q \langle p | \delta \bar{\rho} | q \rangle \langle nq | m p \rangle_{AS} \right\}. \quad (\text{A4})$$

## APPENDIX B

In order to derive the result (13), we work out the matrix element  $\langle n|[T(t), H(\rho_0)]|m\rangle$  using the definition of  $T(t)$ :

$$\begin{aligned}\langle n|[T(t), H(\rho_0)]|m\rangle &= -\frac{c}{\omega^2} A_1(t) \langle n|[p_z, H(\rho_0)]|m\rangle \\ &= -\frac{c}{\omega^2} A_1(t) \int d\vec{r} d\vec{r}' d\vec{r}'' n^*(\vec{r}) \{ \langle \vec{r}|p_z|\vec{r}''\rangle \langle \vec{r}''|H(\rho_0)|\vec{r}'\rangle - \langle \vec{r}|H(\rho_0)|\vec{r}''\rangle \langle \vec{r}''|p_z|\vec{r}'\rangle \} m(\vec{r}'),\end{aligned}$$

where  $a(\vec{r}) = \langle \vec{r}|a\rangle$ . Since the kinetic term in  $H(\rho_0)$  commutes with  $p_z$ , from

$$\langle \vec{r}|p_z|\vec{r}''\rangle = -i(\partial/\partial z)\delta(\vec{r} - \vec{r}'')$$

and the definition of  $H(\rho_0)$  it follows that

$$\begin{aligned}\langle n|[T(t), H(\rho_0)]|m\rangle &= -\frac{c}{\omega^2} A_1(t) \left\{ \langle n|[p_z, U]|m\rangle - i \int d\vec{r} d\vec{r}' n^*(\vec{r}) \right. \\ &\quad \times \left[ \left( \frac{\partial}{\partial z} \frac{1}{|\vec{r} - \vec{r}'|} \right) (\rho_0(\vec{r}', \vec{r}') m(\vec{r}) - \rho_0(\vec{r}, \vec{r}') m(\vec{r}')) \right. \\ &\quad \left. \left. - \frac{1}{|\vec{r} - \vec{r}'|} \left( m(\vec{r}') \frac{\partial}{\partial z} \rho_0(\vec{r}, \vec{r}') - \rho_0(\vec{r}, \vec{r}') \frac{\partial}{\partial z} m(\vec{r}') \right) \right] \right\}.\end{aligned}\quad (\text{B1})$$

From the completeness of the single-particle states  $|p\rangle$  we can write

$$\begin{aligned}\sum_{p,q} \langle nq|mp\rangle_{AS} \langle p|[T(t), \rho_0]|q\rangle &= \sum_q \int d\vec{r} d\vec{r}' n^*(\vec{r}) q^*(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \\ &\quad \times \{ m(\vec{r}) \langle \vec{r}'|[T(t), \rho_0]|q\rangle - m(\vec{r}') \langle \vec{r}|[T(t), \rho_0]|q\rangle \}.\end{aligned}\quad (\text{B2})$$

Since

$$\langle \vec{r}''|[T(t), \rho_0]|q\rangle = \frac{ic}{\omega^2} A_1(t) \left[ \frac{\partial}{\partial z''} \int d\vec{r}'' \rho_0(\vec{r}'', \vec{r}'') q(\vec{r}'') - \int d\vec{r}'' \rho_0(\vec{r}'', \vec{r}'') \frac{\partial}{\partial z''} q(\vec{r}'') \right],$$

Eq. (B2) becomes

$$\begin{aligned}\sum_{p,q} \langle nq|mp\rangle_{AS} \langle p|[T(t), \rho_0]|q\rangle &= \frac{ic}{\omega^2} A_1(t) \sum_q \int d\vec{r} d\vec{r}' d\vec{r}'' n^*(\vec{r}) q(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \\ &\quad \times \left[ m(\vec{r}) \frac{\partial}{\partial z'} \rho_0(\vec{r}', \vec{r}'') - m(\vec{r}) \rho_0(\vec{r}', \vec{r}'') \frac{\partial}{\partial z''} \right. \\ &\quad \left. - m(\vec{r}') \frac{\partial}{\partial z} \rho_0(\vec{r}', \vec{r}'') + m(\vec{r}') \rho_0(\vec{r}, \vec{r}'') \frac{\partial}{\partial z''} \right] q(\vec{r}'').\end{aligned}$$

After exploiting again the completeness of the states  $|p\rangle$  and integrating by part the second term on the right-hand side, we find

$$\begin{aligned}\sum_{p,q} \langle nq|mp\rangle_{AS} \langle p|[T(t), \rho_0]|q\rangle &= \frac{ic}{\omega^2} A_1(t) \left\{ \int d\vec{r} d\vec{r}' n^*(\vec{r}) m(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \left[ \left( \frac{\partial}{\partial z} \rho_0(\vec{r}', \vec{r}'') \right)_{\vec{r}'' \rightarrow \vec{r}'} + \left( \frac{\partial}{\partial z'} \rho_0(\vec{r}', \vec{r}'') \right)_{\vec{r}'' \rightarrow \vec{r}'} \right] \right. \\ &\quad \left. - \int d\vec{r} d\vec{r}' n^*(\vec{r}) m(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \left[ \frac{\partial}{\partial z} \rho_0(\vec{r}, \vec{r}') + \frac{\partial}{\partial z'} \rho_0(\vec{r}, \vec{r}') \right] \right\} \\ &= \frac{ic}{\omega^2} A_1(t) \left\{ \int d\vec{r} d\vec{r}' n^*(\vec{r}) m(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \frac{\partial}{\partial z'} \rho_0(\vec{r}', \vec{r}') \right. \\ &\quad \left. - \int d\vec{r} d\vec{r}' n^*(\vec{r}) m(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \left[ \frac{\partial}{\partial z} \rho_0(\vec{r}, \vec{r}') + \frac{\partial}{\partial z'} \rho_0(\vec{r}, \vec{r}') \right] \right\}.\end{aligned}\quad (\text{B3})$$

From Eqs. (B1) and (B3) one easily obtains

$$\sum_{p,q} \langle nq | m p \rangle_{AS} \langle p | [T(t), \rho_0] | q \rangle - \langle n | [T(t), H(\rho_0)] | m \rangle = \frac{c}{\omega^2} A_1(t) \langle n | [p_x, U] | m \rangle + \frac{ic}{\omega^2} A_1(t) \int d\vec{r} d\vec{r}' n^*(\vec{r}) m(\vec{r}) \frac{\partial}{\partial z'} \left[ \frac{\rho_0(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \right], \quad (\text{B4})$$

from which the result (13) follows since the integral on the right-hand side in Eq. (B4) vanishes.

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<sup>50</sup>The quantity  $4\mu^{(1)+}(\epsilon^{\text{TD}} - \mathbf{V}')\mathbf{D}\Omega^{-2}\mathbf{D}^{-1}(\nabla\mathbf{U})$  can also be recognized as the so-called (static) dipole shielding factor, usually denoted  $\beta_{\infty}$ , times  $Z$  [see for instance, V. G. Kaveeshwar, A. Dalgarno, and R. P. Hurst, *J. Phys. B* **2**, 984 (1969)]. In view of the way  $\xi_{-1}^{(A)}$  arose in our treatment, we have preferred to emphasize its sum-rule character.

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