Polarization propagator calculations of frequency-dependent polarizabilities, Verdet constants, and energy weighted sum rules

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(Received 15 June 1977)

Expressions for the frequency-dependent polarizability, the Verdet constant, and the energy sum rules have been derived consistent through third order in the electronic repulsion using an analytical polarization propagator method. In this approach, the second order optical properties are obtained directly from the propagator without calculating the individual excitation energies and transition moments which appear in the sum-over-states procedures.

I. INTRODUCTION

The perturbation calculation of second order optical properties requires in principle a summation (integration) over an infinite number of excited states which in a square-integrable basis set calculation is approximated by a finite sum over the excited states.[1] Conventional configuration interaction (CI) approaches evaluate the individual excitation energies and transition moments and these methods thus become quite cumbersome, especially when correlation effects are introduced into the calculation (any level of CI beyond the singly excited CI approximation). Direct calculation of the frequency dependent polarizability using the nonvariational Brueckner–Goldstone many-body perturbation theory has been performed by several authors[2,3] and calculations based on formulas, which give strict upper and lower bounds for the frequency dependent polarizability, have recently very successfully been used to calculate polarizabilities for two-electron atoms by Glover and Weinhold.[4] These formulas are however of a degree of complexity which makes accurate calculations of frequency dependent polarizabilities beyond the first excitation threshold and for larger systems very elaborate.

In this communication, we derive formulas for the second order optical properties (frequency-dependent polarizabilities, energy sum rules, and Verdet constants) using an analytical propagator approach.[5,6] The propagator approach allows a direct evaluation of the second order properties without referring to the individual excitation energies and transition moments[5] and correlation effects can therefore efficiently be introduced.

Second order optical properties at the time-dependent Hartree–Fock[7] (TDHF) or coupled Hartree–Fock level of approximation have been reported by a number of workers.[8-13] The TDHF approximation is identical to a polarization propagator approach, which is consistent through first order in electronic repulsion.[14] In this communication we derive formulas for the second order optical properties, based on the polarization propagator which is consistent through *third* order in the electronic repulsion. The formalism straightforwardly can be extended to a polarization propagator which is consistent through any order. In the accompanying publication we report numerical examples.[15]

In the next section we define the polarization propagator and derive the formula for the frequency-dependent polarizability and the even sum rules $S(2K)$, $K=0, \pm, 1, \cdots$. In Sec. III we analyze the calculation of Verdet constants, while the last section contains some concluding remarks.

II. POLARIZABILITIES AND SUM RULES

A. Formal relations

We use the definition of the propagator given by Zubarev.[16] In energy space the spectral form for the propagator is[5]

$$\langle\langle \hat{A}; \hat{B}\rangle\rangle_E = \sum_n \left\{ \frac{\langle 0|\hat{A}|n\rangle\langle n|\hat{B}|0\rangle}{E-\omega_{0n}+i\eta} - \frac{\langle 0|\hat{B}|n\rangle\langle n|\hat{A}|0\rangle}{E+\omega_{0n}-i\eta} \right\}. \quad (1)$$

$|0\rangle$ is the ground state, $|n\rangle$ an excited state, $\omega_{0n}=E_n-E_0$ the exact excitation energy, and $\hat{A}$ and $\hat{B}$ are one-electron operators. Choosing the dipole moment operator, $\hat{\mathrm{R}}$, for $\hat{A}$ and $\hat{B}$ gives[5]

$$-\langle\langle \hat{\mathrm{R}}; \hat{\mathrm{R}}\rangle\rangle_E = 2\sum_{n\neq 0} \frac{\mathrm{R}_{0n}\mathrm{R}_{n0}\omega_{0n}}{\omega_{0n}^2 - E^2}; \ \mathrm{R}_{0n} = \langle 0|\hat{\mathrm{R}}|n\rangle, \quad (2)$$

which is the well-known expression for the real part of frequency-dependent polarizability tensor in the dipole length formulation.[1]

The polarizability tensor in the *PR*, or mixed[17,18] representation can correspondingly be obtained from the propagator $\langle\langle\hat{\mathrm{P}};\hat{\mathrm{R}}\rangle\rangle_E$ ($\hat{\mathrm{P}}$ is the momentum operator) using the equation of motion for the $\langle\langle\hat{\mathrm{R}};\hat{\mathrm{R}}\rangle\rangle_E$ propagator[5] (atomic units)

$$\langle\langle\hat{\mathrm{R}};\hat{\mathrm{R}}\rangle\rangle_E = i\langle\langle\hat{\mathrm{P}};\hat{\mathrm{R}}\rangle\rangle_E/E. \quad (3)$$

In the dipole velocity formulation, the polarizability tensor can be obtained from $\langle\langle\hat{\mathrm{P}};\hat{\mathrm{P}}\rangle\rangle_E$ by considering the equation of motion for $\langle\langle\hat{\mathrm{P}};\hat{\mathrm{R}}\rangle\rangle_E$

$$\langle\langle\hat{\mathrm{R}};\hat{\mathrm{R}}\rangle\rangle_E = \frac{1}{E^2}\{i\langle 0|[\hat{\mathrm{P}},\hat{\mathrm{R}}]|0\rangle + \langle\langle\hat{\mathrm{P}},\hat{\mathrm{P}}\rangle\rangle_E\}$$

$$= \frac{1}{E^2}\{N\,1 + \langle\langle\hat{\mathrm{P}};\hat{\mathrm{P}}\rangle\rangle_E\}, \quad (4)$$

where N is the number of electrons in the system. The term involving N in Eq. (4) dominates over $\langle\langle\hat{\mathrm{P}};\hat{\mathrm{P}}\rangle\rangle_E$ for small E values and Eq. (4) is not suited for the calcula-

 0021-9606/78/6806-2527$01.00

tion of the polarizability tensor in this energy range. The polarizability tensor in the dipole velocity formulation can alternatively be obtained from the propagator $\langle\langle \hat{P};\hat{P}\rangle\rangle_E$ as

$$\frac{1}{E}\frac{d}{dE}\langle\langle \hat{P};\hat{P}\rangle\rangle_E = 4\sum_{n\neq 0}\frac{P_{0n}P_{n0}}{(\omega_{0n}^2-E^2)\omega_{0n}}\left(1+\frac{E^2}{\omega_{0m}^2}+\frac{E^4}{\omega_{0m}^4}+\cdots\right). \tag{5}$$

The first term in Eq. (5) is the polarizability tensor which therefore can be obtained from Eq. (5) for $E \ll \omega_{0m}$. The index m refers to the lowest excitation energy. Equations (2)–(5) express the polarizability tensor in the dipole length, the dipole velocity, and in the mixed formulation. Its spherically symmetric component is known as the frequency-dependent polarizability,[1] $\alpha(E)$, which, e.g., in the dipole-length formulation is expressed as[5]

$$\alpha(E) \equiv -\tfrac{1}{3}\,\mathrm{Tr}\langle\langle \hat{R};\hat{R}\rangle\rangle_E . \tag{6}$$

We next consider the evaluation of the energy weighted sum rules, or moments, directly from the propagator. The symmetric components of the energy weighted sum rules are defined as

$$S(K) = \sum_n f_{0n}\omega_{0n}^K \quad K=0,\pm 1,\pm 2,\ldots, \tag{7}$$

where f_{0n} is the oscillator strength

$$f_{0n}^L = \tfrac{2}{3}|R_{0n}|^2\omega_{0n},$$
$$f_{0n}^V = \tfrac{2}{3}|P_{0n}|^2/\omega_{0n},$$
$$f_{0n}^M = i\,\tfrac{2}{3}\,P_{0n}R_{n0}, \tag{8}$$

in the dipole length (f^L), the dipole velocity (f^V) and in the mixed (f^M) representation, respectively. We refer to the review of Hirschfelder, Byers-Brown, and Epstein[1] for the physical interpretation of the sum rules and note only that $S(0)$ is the Thomas–Reiche–Kuhn sum rule, and that $S(-2)$ is the frequency-independent polarizability.

The even sum rule tensors $S(2K)$, $K=0,\pm 1,\pm 2,\ldots$ can be obtained directly from the propagator by considering the limiting behavior of the propagator for $E\to 0$ and ∞. Using the spectral representation of the propagator one obtains straightforwardly that the even sum rules in the dipole length approximation are given by

$$S^L(2K) = (-1)^K 2^{-K}(K!)^{-1}\lim_{E\to\infty}\left(E^3\frac{d}{dE}\right)^K E^2\langle\langle \hat{R};\hat{R}\rangle\rangle_E , \tag{9}$$

$$S^L(-2K-2) = -2^{-K}(K!)^{-1}\lim_{E\to 0}\left(\frac{1}{E}\frac{d}{dE}\right)^K\langle\langle \hat{R};\hat{R}\rangle\rangle_E , \tag{10}$$

in the dipole velocity form by,

$$S^V(2K+2) = (-1)^K 2^{-K}(K!)^{-1}\lim_{E\to\infty}\left(E^3\frac{d}{dE}\right)^K E^2\langle\langle \hat{P};\hat{P}\rangle\rangle_E , \tag{11}$$

$$S^V(-2K) = -2^{-K}(K!)^{-1}\lim_{E\to 0}\left(\frac{1}{E}\frac{d}{dE}\right)^K\langle\langle \hat{P};\hat{P}\rangle\rangle_E , \tag{12}$$

and in the mixed representation by

$$S^M(2K) = i(-1)^K 2^{-K}(K!)^{-1}\lim_{E\to\infty}\left(E^3\frac{d}{dE}\right)^K E\langle\langle \hat{P};\hat{R}\rangle\rangle_E , \tag{13}$$

$$S^M(-2K-2) = -i\,2^{-K}(K!)^{-1}\lim_{E\to 0}\left(\frac{1}{E}\frac{d}{dE}\right)^K\frac{1}{E}\langle\langle \hat{P};\hat{R}\rangle\rangle , \tag{14}$$

where $K=0,1,2,\ldots$. The odd sum rules cannot be obtained by this procedure because the propagator (2) is an even function of E.

B. Third order expressions

We have previously[14] derived an analytical expression for the polarization propagator on TDHF form which is consistent through third order in the electronic repulsion. In this section, we use this propagator to obtain explicit third order expression for the frequency-dependent polarizability tensor and the energy sum rule tensor.

Let $\{u_i\}$ be a set of Hartree–Fock (HF) orbitals and let indices $\alpha,\beta,\gamma,\delta$ (m,n,p,q) refer to occupied (unoccupied) orbitals and $i,j,k,1$ to unspecified orbitals. The HF orbitals define a set of annihilation and creation operators $\{a_i\}$, $\{a_i^\dagger\}$ which together define a set of spin-adapted particle–hole operators

$${}^1Q_{m\alpha}^\dagger = \frac{1}{\sqrt{2}}(a_{m+}^\dagger a_{\alpha+} + a_{m-}^\dagger a_{\alpha-})\ (S=0,\ M_S=0)$$
$${}^3Q_{m\alpha}^\dagger = \frac{1}{\sqrt{2}}(a_{m+}^\dagger a_{\alpha+} - a_{m-}^\dagger a_{\alpha-})\ (S=1,\ M_S=0). \tag{15}$$

We arrange the spin-adapted particle–hole operators in super row vectors ${}^1\mathbf{Q}$ and ${}^3\mathbf{Q}$. The position and momentum operators can be expressed in terms of the super row vectors as

$$\hat{R} = \sum_{ij} r_{ij}a_i^\dagger a_j = \sqrt{2}\,(\mathbf{r},\mathbf{r})\begin{pmatrix}{}^1\tilde{\mathbf{Q}}\\ {}^1\tilde{\mathbf{Q}}^\dagger\end{pmatrix} \tag{16}$$

$$\hat{P} = \sum_{ij} p_{ij}a_i^\dagger a_j = -\sqrt{2}\,(\mathbf{p},-\mathbf{p})\begin{pmatrix}{}^1\tilde{\mathbf{Q}}\\ {}^1\tilde{\mathbf{Q}}^\dagger\end{pmatrix}, \tag{17}$$

where

$$r_{ij} = \langle u_i|\hat{R}|u_j\rangle , \tag{18}$$

${}^1\tilde{\mathbf{Q}}$ is the transpose of ${}^1\mathbf{Q}$, and $\mathbf{r}$ is a row vector with elements $r_{m\alpha}$. In deriving Eqs. (16) and (17) we have used the fact that the operator space $\{a_i^\dagger a_j\}$ is spanned by the particle–hole and hole–particle super row operators alone. Using Eqs. (16) and (17), the propagators $\langle\langle \hat{R};\hat{R}\rangle\rangle_E$, $\langle\langle \hat{P};\hat{R}\rangle\rangle_E$, and $\langle\langle \hat{P};\hat{P}\rangle\rangle_E$ take the form

$$\langle\langle \hat{R};\hat{R}\rangle\rangle_E = 2(\mathbf{r},\mathbf{r})\,{}^1\mathbf{P}(E)\begin{pmatrix}\tilde{\mathbf{r}}\\ \tilde{\mathbf{r}}\end{pmatrix} \tag{19}$$

$$\langle\langle \hat{P};\hat{R}\rangle\rangle_E = -2(\mathbf{p},-\mathbf{p})\,{}^1\mathbf{P}(E)\begin{pmatrix}\tilde{\mathbf{r}}\\ \tilde{\mathbf{r}}\end{pmatrix} \tag{20}$$

$$\langle\langle \hat{P};\hat{P}\rangle\rangle_E = -2(\mathbf{p},-\mathbf{p})\,{}^1\mathbf{P}(E)\begin{pmatrix}\tilde{\mathbf{p}}\\ -\tilde{\mathbf{p}}\end{pmatrix}, \tag{21}$$

where

$$ {}^{1}\mathbf{P}(E)=\begin{Bmatrix} \langle\langle {}^{1}\tilde{\mathbf{Q}};{}^{1}\mathbf{Q}^{\dagger}\rangle\rangle_E & \langle\langle {}^{1}\tilde{\mathbf{Q}};{}^{1}\mathbf{Q}\rangle\rangle_E \\ \langle\langle {}^{1}\tilde{\mathbf{Q}}^{\dagger};{}^{1}\mathbf{Q}^{\dagger}\rangle\rangle_E & \langle\langle {}^{1}\tilde{\mathbf{Q}}^{\dagger};{}^{1}\mathbf{Q}\rangle\rangle_E \end{Bmatrix}=\begin{Bmatrix} \mathbf{P}_{11}(E) & \mathbf{P}_{12}(E) \\ \mathbf{P}_{21}(E) & \mathbf{P}_{22}(E) \end{Bmatrix}. \tag{22} $$

Notice that the particle–hole part of the polarization propagator alone is not sufficient for direct calculation of second order optical properties.

In a previous paper,[14] we showed that the propagator $\mathbf{P}(E)$ could be obtained consistent to third order in the form

$$ \mathbf{P}(E)=\begin{Bmatrix} E\mathbf{1}-\mathbf{A}-\tilde{\mathbf{C}}(E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C} & -\mathbf{B} \\ -\mathbf{B}^* & -E\mathbf{1}-\mathbf{A}^*-\mathbf{C}^{\dagger}(-E\mathbf{1}-\mathbf{D}^*)^{-1}\mathbf{C}^* \end{Bmatrix}^{-1}. \tag{23} $$

In the following, we assume that the matrices **A**, **B**, **C**, and **D** are real. Explicit expressions for the matrix elements can be found in Ref. (14). When the terms involving C and D are absent, the propagator has the TDHF form, and the usual eigenproblem solution for it generates immediately the spectral representation,[19] allowing straightforward sum-over-states evaluation of second order properties. The energy dependence in the terms $\tilde{\mathbf{C}}(E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C}$ and $\tilde{\mathbf{C}}(-E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C}$, which arise from two-particle, two-hole $(2p-2h)$ excitations,[20] prevents reduction of (23) to a simple eigenvalue problem. We have recently[21] discussed the calculation of individual excitation energies from a propagator of the form in Eq. (23).

The frequency-dependent polarizability can however be calculated directly from the propagator[5] in Eq. (23) without explicit knowledge of the individual excitation energies. The frequency, E_0, at which the polarizability is wanted must be inserted in Eq. (23), and $\langle\langle\hat{\mathbf{R}};\hat{\mathbf{R}}\rangle\rangle_{E_0}$, $\langle\langle\hat{\mathbf{P}};\hat{\mathbf{R}}\rangle\rangle_{E_0}$, and $\langle\langle\hat{\mathbf{P}};\hat{\mathbf{P}}\rangle\rangle_{E_0}$ can then be calculated from Eqs. (19)–(22). From Eqs. (2)–(5) we obtain expressions for the frequency-dependent polarizability in the dipole length, dipole velocity, and mixed representations:

$$ \alpha^L(E)=-\tfrac{2}{3}\,\mathrm{Tr}\{\mathbf{r}(\mathbf{P}_{11}+\mathbf{P}_{12}+\mathbf{P}_{21}+\mathbf{P}_{22})\tilde{\mathbf{r}}\} \tag{24} $$

$$ \alpha^V(E)=(\tfrac{2}{3}\,\mathrm{Tr}\{\mathbf{p}(\mathbf{P}_{11}-\mathbf{P}_{12}-\mathbf{P}_{21}+\mathbf{P}_{22})\tilde{\mathbf{p}}\}-N)/E^2 \tag{25} $$

$$ \alpha^M(E)=\frac{2i}{3E}\,\mathrm{Tr}\{\mathbf{p}(\mathbf{P}_{11}+\mathbf{P}_{12}-\mathbf{P}_{21}-\mathbf{P}_{22})\tilde{\mathbf{r}}\}. \tag{26} $$

The energy sum rules in a third order theory can now be calculated from Eqs. (9)–(14) by differentiating the propagator matrix (23) with respect to E and considering the limits for $E\to\infty$ and $E\to 0$. We consider first the limit $E\to\infty$ and divide for convenience the propagator matrix into a part that contains the TDHF-like matrix and a residual term

$$ \mathbf{P}(E)=\left\{\begin{pmatrix} E\mathbf{1}-\mathbf{A} & -\mathbf{B} \\ -\mathbf{B} & -E\mathbf{1}-\mathbf{A}\end{pmatrix} -\begin{pmatrix} \tilde{\mathbf{C}}(E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C} & 0 \\ 0 & \tilde{\mathbf{C}}(-E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C}\end{pmatrix}\right\}^{-1}. \tag{27} $$

Expanding the first part into a power series in E^{-1}, we obtain

$$ \begin{pmatrix} E\mathbf{1}-\mathbf{A} & -\mathbf{B} \\ -\mathbf{B} & -E\mathbf{1}-\mathbf{A}\end{pmatrix}^{-1}=\sum_{n=0}^{\infty}E^{-n-1}\,\mathbf{f}(n), \tag{28} $$

where

$$ \mathbf{f}(n)=\begin{cases} \frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1&1\\1&1\end{pmatrix}\begin{pmatrix}(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B}) & 0\\ 0 & (\mathbf{A}-\mathbf{B})(\mathbf{A}+\mathbf{B})\end{pmatrix}^{n/2}\begin{pmatrix}1&1\\1&-1\end{pmatrix} & n \text{ even}, \\ \frac{1}{2}\begin{pmatrix}1&1\\1&-1\end{pmatrix}\begin{pmatrix}\mathbf{A}-\mathbf{B}&0\\0&\mathbf{A}+\mathbf{B}\end{pmatrix}\begin{pmatrix}(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B}) & 0\\ 0 & (\mathbf{A}-\mathbf{B})(\mathbf{A}+\mathbf{B})\end{pmatrix}^{\frac{n-1}{2}}\begin{pmatrix}1&1\\1&-1\end{pmatrix} & n \text{ odd}. \end{cases} \tag{29} $$

A similar expansion of the second part in Eq. (27) gives

$$ \begin{pmatrix} \tilde{\mathbf{C}}(E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C} & 0 \\ 0 & \tilde{\mathbf{C}}(-E\mathbf{1}-\mathbf{D})^{-1}\mathbf{C}\end{pmatrix}=\sum_{n=0}^{\infty}E^{-n-1}\mathbf{h}(n), \tag{30} $$

where

$$ \mathbf{h}(n)=\begin{pmatrix}\tilde{\mathbf{C}}\mathbf{D}^n\mathbf{C} & 0\\ 0 & (-1)^{n+1}\tilde{\mathbf{C}}\mathbf{D}^n\mathbf{C}\end{pmatrix}. \tag{31} $$

The propagator matrix in Eq. (27) can thus be expressed in powers of E^{-1}. To obtain the sum rules, we need to apply the differential operator from Eq. (9), $[E^3(d/dE)]^K E^2$ to $(1,\pm 1)\mathbf{P}(E)\binom{1}{\pm 1}$. We find

$$ (-1)^K 2^{-K}(K!)^{-1}\lim_{E\to\infty}\left(E^3\frac{d}{dE}\right)^K E^2(1,\pm 1)\mathbf{P}(E)\begin{pmatrix}1\\ \pm 1\end{pmatrix} =(1,\pm 1)\sum_{j=0}^{K}\sum_{n_1,n_2,\ldots,n_{2j+1}} \times\mathbf{f}(n_1)\prod_{l=1}^{j}\mathbf{h}(n_{2l})\,\mathbf{f}(n_{2l+1})\begin{pmatrix}1\\ \pm 1\end{pmatrix}, \tag{32} $$

where the n_k represent partitions of the integers the sum of which must fulfill

$$\sum_{k=1}^{2j+1} n_k = 2K+1-2j;\; n_k \geq 0\,. \tag{33}$$

This relation significantly limits the number of terms in the product. The expansion of $[E^3(d/dE)]^K E^2 \mathbf{P}(E)$ contains a term which is proportional to E and could make the series divergent. This term is however removed by the left and right multiplication with (1 ± 1) before taking the limit $E \to \infty$. Equation (32), combined with Eqs. (9) and (11), allows us to calculate the positive even sum rules $\mathbf{S}^L(2K)$ and $\mathbf{S}^V(2K+2)$, and the simplest cases will be given explicitly later.

To calculate the sum rules for negative K, we consider the limiting behavior of the propagator for $E \to 0$. The propagator matrix is then divided up as

$$\mathbf{P}(E) = \left\{\begin{pmatrix} E\mathbf{1} - \mathbf{A} + \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C} & -\mathbf{B} \\ -\mathbf{B} & -E\mathbf{1} - \mathbf{A} + \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C} \end{pmatrix} - \begin{pmatrix} \tilde{\mathbf{C}}(E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C} & 0 \\ 0 & \tilde{\mathbf{C}}(-E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C} \end{pmatrix}\right\}^{-1}. \tag{34}$$

By defining $\mathbf{A}' = \mathbf{A} - \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C}$, the first term in Eq. (34) can be expanded in powers of E,

$$\begin{pmatrix} E\mathbf{1} - \mathbf{A}' & \mathbf{B} \\ \mathbf{B} & -E\mathbf{1} - \mathbf{A}' \end{pmatrix}^{-1} = -\sum_{n=1}^{\infty} E^{n-1}\mathbf{g}(n)\,, \tag{35}$$

where

$$\mathbf{g}(n) = \begin{cases} \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} (\mathbf{A}'-\mathbf{B})^{-1}(\mathbf{A}'+\mathbf{B})^{-1} & 0 \\ 0 & (\mathbf{A}'+\mathbf{B})^{-1}(\mathbf{A}'-\mathbf{B})^{-1} \end{pmatrix}^{\frac{n}{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} & n \text{ even} \\[2ex] \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} (\mathbf{A}'+\mathbf{B})^{-1} & 0 \\ 0 & (\mathbf{A}'-\mathbf{B})^{-1} \end{pmatrix}\begin{pmatrix} (\mathbf{A}'-\mathbf{B})^{-1}(\mathbf{A}'+\mathbf{B})^{-1} & 0 \\ 0 & (\mathbf{A}'+\mathbf{B})^{-1}(\mathbf{A}'-\mathbf{B})^{-1} \end{pmatrix}^{\frac{n-1}{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} & n \text{ odd}\,. \end{cases} \tag{36}$$

We can similarly expand the last term in Eq. (34) in powers of E, obtaining

$$\begin{pmatrix} \tilde{\mathbf{C}}(E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C} & 0 \\ 0 & \tilde{\mathbf{C}}(-E\mathbf{1} - \mathbf{D})^{-1}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}^{-1}\mathbf{C} \end{pmatrix} = -\sum_{n=2}^{\infty} E^{n-1}\mathbf{k}(n)\,, \tag{37}$$

where

$$\mathbf{k}(n) = \begin{pmatrix} \tilde{\mathbf{C}}\mathbf{D}^{-n}\mathbf{C} & 0 \\ 0 & (-1)^{n+1}\tilde{\mathbf{C}}\mathbf{D}^{-n}\mathbf{C} \end{pmatrix}. \tag{38}$$

The propagator matrix can now be expressed in powers of E, and the negative sum rules are obtained by considering the effect of the operator $(1/E)(d/dE)^K$ on $\mathbf{P}(E)$. We find

$$-2^{-K}(K!)^{-1}\lim_{E\to 0}(1, \pm 1)\mathbf{P}(E)\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix} = (1, \pm 1)\sum_{j=0}^{2K}\sum_{n_1, n_2, \ldots, n_{2j+1}} \times \mathbf{g}(n_1)\prod_{l=1}^{j}\mathbf{k}(n_{2l})\mathbf{g}(n_{2l+1})\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}, \tag{39}$$

where the n_k's are restricted to those which fulfill

$$\sum_{k=1}^{2j+1} n_k = 2K+1+2j;\; n_{2k} \geq 2 \text{ and } n_{2k+1} \geq 1\,. \tag{40}$$

The number of terms in the product is thus again limited, and the divergent term in $(1/E)(d/dE)^K\mathbf{P}(E)$ which is proportional to E^{-1} vanishes from left and right multiplication with (1 ± 1) before the limit $E \to 0$ is taken. Eq. (39) combined with Eqs. (10) and (12) then gives the negative even sum rules $\mathbf{S}^L(-2K^{-2})$ and $\mathbf{S}^V(-2K)$.

An analysis similar to the one made above can be carried out in the mixed representation, but for brevity, we omit the general results and give below explicit forms only for some cases of special interest. The S(2) sum rule tensors are found from the above analysis to be

$$\mathbf{S}^L(2) = -4\mathbf{r}[(\mathbf{A}-\mathbf{B})(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B}) + (\mathbf{A}-\mathbf{B})\tilde{\mathbf{C}}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{C}(\mathbf{A}-\mathbf{B})]\tilde{\mathbf{r}}\,, \tag{41}$$

$$\mathbf{S}^V(2) = -4\mathbf{p}(\mathbf{A}+\mathbf{B})\tilde{\mathbf{p}}\,, \tag{42}$$

$$\mathbf{S}^M(2) = 4i\mathbf{p}[(\mathbf{A}+\mathbf{B})(\mathbf{A}-\mathbf{B}) + \tilde{\mathbf{C}}\mathbf{C}]\tilde{\mathbf{r}}\,, \tag{43}$$

and correspondingly for S(0) we have

$$\mathbf{S}^L(0) = 4\,\mathbf{r}(\mathbf{A}-\mathbf{B})\,\tilde{\mathbf{r}}\,, \tag{44}$$

$$\mathbf{S}^V(0) = -4\,\mathbf{p}(\mathbf{A}'-\mathbf{B})^{-1}\tilde{\mathbf{p}}\,, \tag{45}$$

$$\mathbf{S}^M(0) = -4i\,\mathbf{p}\tilde{\mathbf{r}}\,. \tag{46}$$

The results for S(−2) are

$$\mathbf{S}^L(-2) = 4\,\mathbf{r}(\mathbf{A}'+\mathbf{B})^{-1}\tilde{\mathbf{r}}\,, \tag{47}$$

$$\mathbf{S}^V(-2) = -4\mathbf{p}(\mathbf{A}'-\mathbf{B})^{-1}[(\mathbf{A}'+\mathbf{B})^{-1} + (\mathbf{A}'+\mathbf{B})^{-1}\tilde{\mathbf{C}}\mathbf{D}^{-2}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}^{-2}\mathbf{C}(\mathbf{A}'+\mathbf{B})^{-1} + \tilde{\mathbf{C}}\mathbf{D}^{-2}\mathbf{C}(\mathbf{A}'+\mathbf{B})^{-1}\tilde{\mathbf{C}}\mathbf{D}^{-2}\mathbf{C} + \tilde{\mathbf{C}}\mathbf{D}^{-3}\mathbf{C}](\mathbf{A}'-\mathbf{B})^{-1}\tilde{\mathbf{p}} \tag{48}$$

$$\mathbf{S}^M(-2) = -4i\mathbf{p}(\mathbf{A}'+\mathbf{B})^{-1}[1 + \tilde{\mathbf{C}}\mathbf{D}^{-2}\mathbf{C}](\mathbf{A}'+\mathbf{B})^{-1}\tilde{\mathbf{r}}\,. \tag{49}$$

We note that $S^V(2)$ and $S^L(0)$ do not depend on the two-particle, two-hole correction at all, and that $S^V(0)$ and $S^L(-2)$ only require knowledge of the frequency-independent part of the $2p-2h$ matrix. Furthermore, Eq. (46) exhibits the peculiarity of the mixed representation that $S^M(0)$ is independent of the approximation used for the propagator.[22] In TDHF (a first order polarization propagator approximation), the sum rules become especially simple, since the $2p$-$2h$ terms disappear, and only positive or negative powers of A+B remain in Eqs. (41)–(49). Examples have been given by Linderberg and Öhrn.[5] In such a case, the sum rules can of course be obtained unambiguously from the eigenproblem solution and the sum-over-states formula, Eq. (7).

III. THE VERDET CONSTANT

A magnetic field applied parallel to the direction of propagation of incident light produces a rotation of the plane of polarization. This is known as the Faraday effect.[23] The magnitude of the angle of rotation per unit length and unit pressure is determined by the magnetic field and the Verdet constant, which is given approximately by the Becquerel formula[24,25]

$$V(E)=\frac{e}{2mc^2}E\,\frac{dn(E)}{dE}\ \text{rad Oe}^{-1}\ \text{atm}^{-1}\ \text{cm}^{-1}, \qquad (50)$$

where $n(E)$ is the refractive index defined through the relation[26]

$$\frac{n^2(E)-1}{n^2(E)+2}=\tfrac{4}{3}\pi N\alpha(E) \qquad (51)$$

and N is the number density of atoms or molecules. In the gas phase where $n(E)\approx 1$ Eq. (51) reduces to

$$n(E)=1+2\pi N\alpha(E) \qquad (52)$$

and $N=2.68811\times 10^{19}$ molecules atm^{-1} cm^{-3}.

The Verdet constant then becomes

$$V(E)=\frac{\pi e N}{mc^2}E\,\frac{d\alpha(E)}{dE} \qquad (53)$$

and converting from radians to μ(arc) min, we obtain the units in which the Verdet constant is normally expressed,[27]

$$V(E)=1.0800\times 10^6 N\,\frac{e}{mc^2}E\,\frac{d\alpha(E)}{dE}\ \mu\text{min Oe}^{-1}\ \text{atm}^{-1}\ \text{cm}^{-1} \qquad (54)$$

or

$$V(E)=25.2864\,E\,\frac{d\alpha(E)}{dE}\ \mu\text{min Oe}^{-1}\ \text{atm}^{-1}\ \text{cm}^{-1} \qquad (55)$$

with E and $\alpha(E)$ given in atomic units. According to Eqs. (2)–(5) and (19)–(21) the quantity needed to evaluate $d\alpha(E)/dE$ is

$$\frac{d}{dE}\mathbf{P}(E)=-\mathbf{P}(E)\begin{pmatrix}1+\tilde{\mathbf{C}}(E1-\mathbf{D})^{-2}\mathbf{C} & 0\\ 0 & -1-\tilde{\mathbf{C}}(E1+\mathbf{D})^{-2}\mathbf{C}\end{pmatrix}\mathbf{P}(E), \qquad (56)$$

where we have used the expression for the propagator matrix $P(E)$ in Eq. (23), and the result that the derivative of an inverse matrix with respect to a parameter is given by

$$\frac{d\mathbf{M}(x)^{-1}}{dx}=-\mathbf{M}(x)^{-1}\frac{d\mathbf{M}(x)}{dx}\mathbf{M}(x)^{-1}. \qquad (57)$$

This relation follows from differentiation of $\mathbf{M}\mathbf{M}^{-1}=1$.

Using Eqs. (2), (6), (19), (22), and (55) gives the following expression for the Verdet constant in the dipole length formulation

$$\begin{aligned}V^L(E)=16.8576E\,\mathrm{Tr}\{&\mathbf{r}\\ &\times[(\mathbf{P}_{11}+\mathbf{P}_{21})(1+\tilde{\mathbf{C}}(E1-\mathbf{D})^{-2}\mathbf{C})(\mathbf{P}_{11}+\mathbf{P}_{12})\\ &-(\mathbf{P}_{12}+\mathbf{P}_{22})(1+\tilde{\mathbf{C}}(E1+\mathbf{D})^{-2}\mathbf{C})(\mathbf{P}_{21}+\mathbf{P}_{22})]\tilde{\mathbf{r}}\}.\end{aligned} \qquad (58)$$

The Verdet constant (same units) in the dipole velocity form is equivalently obtained from Eqs. (4), (21), (22), (55), and (56) as

$$\begin{aligned}V_t^V(E)=-16.8576\,\frac{1}{E}\,\mathrm{Tr}\{&\mathbf{p}\\ &\times[(\mathbf{P}_{11}-\mathbf{P}_{21})(1+\tilde{\mathbf{C}}(E1-\mathbf{D})^{-2}\mathbf{C})(\mathbf{P}_{11}-\mathbf{P}_{12})-(\mathbf{P}_{12}-\mathbf{P}_{22})\\ &\times(1+\tilde{\mathbf{C}}(E1+\mathbf{D})^{-2}\mathbf{C})(\mathbf{P}_{21}-\mathbf{P}_{22})]\tilde{\mathbf{p}}\}+3\alpha^V(E)],\end{aligned} \qquad (59)$$

where $\alpha^V(E)$ is the spherically symmetric component of the frequency-dependent polarizability in the dipole velocity formulation. To obtain the Verdet constant in the mixed representation, we differentiate Eq. (3) with respect to E and use Eqs. (20) and (55)–(56), which gives

$$\begin{aligned}V^M(E)=-16.8576[i\,\mathrm{Tr}\{&\mathbf{p}\\ &\times[(\mathbf{P}_{11}-\mathbf{P}_{21})(1+\tilde{\mathbf{C}}(E1-\mathbf{D})^{-2}\mathbf{C})(\mathbf{P}_{11}+\mathbf{P}_{12})-(\mathbf{P}_{12}-\mathbf{P}_{22})\\ &\times(1+\tilde{\mathbf{C}}(E1+\mathbf{D})^{-2}\mathbf{C})(\mathbf{P}_{21}+\mathbf{P}_{22})]\tilde{\mathbf{r}}\}+3\alpha^M(E)].\end{aligned} \qquad (60)$$

Explicit formulas for the Verdet constant have thus been derived in the dipole velocity, and the mixed representation.

IV. SUMMARY

Formulas for the calculation of frequency-dependent polarizabilities, Verdet constants, and the energy weighted sum rules have been derived from a polarization propagator which is consistent through third order in the electronic repulsion. Extensions to polarization propagators which are consistent through an arbitrary order are straightforward since all that is required is a redefinition of the matrices in the propagator (23). Knowledge of individual excitation energies is not necessary in the calculations which make this approach particularly useful for introducing correlation into the calculation of second order optical properties. Results in the dipole length, the dipole velocity, and the mixed representation are obtained with no additional effort.

The Thomas–Reiche–Kuhn sum rule in the mixed formulation shows the peculiarity of being independent of the approximation made to the propagator and is thus only dependent on the basis set used in the calculation.[22]

In the following paper[15] we present numerical examples of the applications of the derived expression. Examples will include the He and Be atom and the CO, FH, and CH^+ molecules.

ACKNOWLEDGMENTS

We wish to thank Jack Simons and Jan Linderberg for illuminating discussions. This work was supported in part by NATO Research Grant No. 1103 (1975). One of us (JO) would like to thank the Danish Natural Science Research Council for financial support.

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[1] J. O. Hirschfelder, W. Byers–Brown, and S. T. Epstein, Adv. Quantum Chem. **1**, 255 (1964).
[2] H. P. Kelly, Phys. Rev. B **136**, 896 (1964).
[3] N. C. Dutta, T. Ishihara, C. Matsubara, and T. P. Das, Phys. Rev. Lett. **22**, 8 (1969).
[4] R. M. Glover and F. Weinhold, J. Chem. Phys. **65**, 4913 (1976).
[5] J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic, London, 1973).
[6] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York, 1974).
[7] P. Jørgensen, Ann. Rev. Phys. Chem. **26**, 359 (1975).
[8] A. Dalgarno and J. T. Lewis, Proc. R. Soc. London Ser. A **223**, 70 (1955).
[9] R. F. Stewart, D. K. Watson, and A. Dalgarno, J. Chem. Phys. **63**, 3222 (1975).
[10] D. K. Watson, R. F. Stewart, and A. Dalgarno, J. Chem. Phys. **64**, 4995 (1976).
[11] P. H. S. Martin, W. H. Henneker, and V. McKoy, Chem. Phys. Lett. **27**, 52 (1974) and J. Chem. Phys. **62**, 69 (1975).
[12] I. R. Epstein, J. Chem. Phys. **53**, 1881 (1970).
[13] J. Oddershede, P. Jørgensen, and N. H. F. Beebe, J. Chem. Phys. **63**, 2996 (1975).
[14] J. Oddershede and P. Jørgensen, J. Chem. Phys. **66**, 1541 (1977).
[15] P. Jørgensen, J. Oddershede, P. Albertsen, and N. H. F. Beebe, J. Chem. Phys. **68**, 0000 (1978), the following paper.
[16] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [Sov. Phys. Usp. **3**, 320 (1960)].
[17] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of one- and two-electron atoms* (Springer, Berlin, 1957).
[18] Aa. E. Hansen, Mol. Phys. **13**, 425 (1967).
[19] P. Jørgensen and J. Linderberg, Int. J. Quantum Chem. **4**, 587 (1970).
[20] P. Jørgensen, J. Oddershede, and M. Ratner, Chem. Phys. Lett. 32, 111 (1975).
[21] J. Oddershede, P. Jørgensen, and N. H. F. Beebe, Int. J. Quantum Chem. (to be published).
[22] Aa. E. Hansen and T. D. Bouman, Chem. Phys. Lett. **45**, 326 (1977).
[23] R. Serber, Phys. Rev. **41**, 489 (1932).
[24] H. Becquerel, C. R. Acad. Sci. **125**, 679 (1897).
[25] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University, Oxford, 1932).
[26] J. O. Hirschfelder, C. F. Curtis, and R. F. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
[27] L. R. Ingersoll and D. H. Liebenberg, J. Opt. Soc. Am. **46**, 538 (1956).