Electric and magnetic nuclear shielding tensors: A study of the water molecule

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(Received 18 December 1985)

We introduce a series of new linear-response tensors which enable one to estimate the actual electric and magnetic fields at the nuclei of a molecule immersed in an external, spatially uniform, periodical electromagnetic field. The analysis is extended to the case of an electric field gradient. These tensors may be called electromagnetic nuclear shieldings. They possess interesting properties and fulfill a series of general sum rules and equations, showing the deep relations among the electromagnetic properties of molecules. An accurate numerical test has been performed on the water molecule, with use of the random-phase approximation to decouple the polarization propagator equations.

I. INTRODUCTION

In previous papers we have introduced the idea of static[1] and dynamic[2] electric shielding at the nuclei of a molecule immersed in a spatially uniform external electric field.[3-8] We have also shown the general relations existing between the electric shielding and other second-order molecular properties, namely electric polarizability, magnetic susceptibility, force constants, and infrared intensity.[9,10] The present paper is aimed at generalizing the concept of nuclear shielding in the presence of electromagnetic radiation: to this end the idea of dynamic electromagnetic shielding tensors is introduced.

Using infinitesimal canonical transformations of the time-dependent Hamiltonian, and the related off-diagonal hypervirial relations,[11] a series of quantum-mechanical sum rules can be proven, showing that the electric and magnetic properties of molecules are deeply interconnected.

The new tensors are examined in Sec. II. Section III shows that the electromagnetic shieldings can be given a complex representation, which may be useful to study absorption and emission processes. The effects of an electric field gradient are analyzed in Sec. IV. The results of an extended basis calculations on the water molecule are discussed in Sec. V.

II. THEORY

Let $\Psi_j^0 \equiv |j\rangle$, $j=0,1,2,\ldots$, be the eigenfunctions of the clamped-nuclei, time-independent Hamiltonian H_0 of a molecule having n electrons, with coordinates $\mathbf{r}_i$, canonical momenta $\mathbf{p}_i$, $i=1,2,\ldots,n$, charge $-e$, and N nuclei, with coordinates $\mathbf{R}_I$, charge $Z_I e$, $I=1,2,\ldots,N$. In the presence of electromagnetic radiation, the first-order time-dependent Hamiltonians, within the length and angular momentum gauges, are written

$$H^{\mathrm{E}}=\mathbf{h}^{\mathrm{E}}\cdot\mathbf{E}(\mathbf{r},\omega),\quad \mathbf{E}=\mathbf{E}_0\cos\left[\omega\left[t-\frac{\mathbf{k}\cdot\mathbf{r}}{c}\right]\right], \tag{1}$$

$$\mathbf{h}^{\mathrm{E}}=-\boldsymbol{\mu}=e\mathbf{R}, \tag{2}$$

$$\mathbf{R}=\sum_{i=1}^{n}\mathbf{r}_i, \tag{3}$$

$$H^{\mathrm{B}}=\mathbf{h}^{\mathrm{B}}\cdot\mathbf{B}(\mathbf{r},\omega),\quad \mathbf{B}=\mathbf{k}\times\mathbf{E}, \tag{4}$$

$$\mathbf{h}^{\mathrm{B}}=-\mathbf{m}=\frac{e}{2mc}\mathbf{L}, \tag{5}$$

$$\mathbf{L}=\sum_{i=1}^{n}l_i,\quad l_i=\mathbf{r}_i\times\mathbf{p}_i, \tag{6}$$

retaining the notation of a previous paper.[11] $\mathbf{E},\mathbf{B}$ are the electric and magnetic vectors of the perturbing radiation, a monochromatic linearly polarized plane wave traveling in the direction of the unit vector $\mathbf{k}$. Within the dipole approximation the fields are spatially uniform over the molecular dimensions, and can be put equal to the value they have at the origin of the coordinate system:

$$\mathbf{E}(\mathbf{r},\omega)\simeq\mathbf{E}(\mathbf{0},\omega), \tag{7}$$

$$\mathbf{B}(\mathbf{r},\omega)\simeq\mathbf{B}(\mathbf{0},\omega). \tag{8}$$

We recall that the dipole approximation can be justified for wavelengths much larger than the molecular size. In some cases, however, this limitation is physically meaningless and must be relaxed, including also multipole terms in (1).

We will be interested in the average values, correct through first order in the perturbing radiation, of operators T which may themselves involve the perturbation, thus, in obvious notation,

$$T=T_0+T_1+\cdots.$$

From propagator theory,[12] or, equivalently, from time-dependent perturbation theory,[13,14] the general expression for the diagonal matrix elements of such an observable in the perturbed state Ψ_a is then, correct through first order,

$$\langle T\rangle_a=\langle a\mid T_0\mid a\rangle+\langle a\mid T_1\mid a\rangle+\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\,\omega_{ja}\mathrm{Re}(\langle a\mid T_0\mid j\rangle\langle j\mid \boldsymbol{\mu}\mid a\rangle)\cdot\mathbf{E}+\omega_{ja}\mathrm{Re}(\langle a\mid T_0\mid j\rangle\langle j\mid \mathbf{m}\mid a\rangle\cdot\mathbf{B}$$
$$-\mathrm{Im}(\langle a\mid T_0\mid j\rangle\langle j\mid \boldsymbol{\mu}\mid a\rangle)\cdot\dot{\mathbf{E}}-\mathrm{Im}(\langle a\mid T_0\mid j\rangle\langle j\mid \mathbf{m}\mid a\rangle)\cdot\dot{\mathbf{B}}]\;, \tag{9}$$

using the Gaussian unit system. In (9) $\dot{\mathbf{E}},\dot{\mathbf{B}}$ are partial derivatives with respect to time. The quantity

$$\Delta\langle T\rangle_a=\langle T\rangle_a-\langle a\mid T_0\mid a\rangle \tag{10}$$

is the contribution to the observable induced by the electromagnetic radiation, adding to the permanent value $\langle a\mid T_0\mid a\rangle$.

The electric dipole moment is $\boldsymbol{\mu}=\boldsymbol{\mu}_0$ and therefore, from (9) and (10), the expression for the induced electric dipole moment in the perturbed state Ψ_a (the subindex a is omitted to avoid cumbersome notation) is

$$\Delta\langle\boldsymbol{\mu}\rangle=\boldsymbol{\alpha}\cdot\mathbf{E}+\boldsymbol{\kappa}\cdot\mathbf{B}+\hat{\boldsymbol{\alpha}}\cdot\dot{\mathbf{E}}+\hat{\boldsymbol{\kappa}}\cdot\dot{\mathbf{B}}\;, \tag{11}$$

where[15]

$$\boldsymbol{\alpha}(\omega)=\frac{e^2}{\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\mid\mathbf{R}\mid j\rangle\langle j\mid\mathbf{R}\mid a\rangle) \tag{12}$$

is the electric dipole polarizability (a symmetric polar tensor of dimension l^3) in the length formalism,

$$\hat{\boldsymbol{\kappa}}(\omega)=-\frac{e^2}{2cm\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\mathrm{Im}(\langle a\mid\mathbf{R}\mid j\rangle\langle j\mid\mathbf{L}\mid a\rangle) \tag{13}$$

is related to the optical activity,[15] and will be called hereafter optical activity tensor in the length—angular-momentum formalism (an axial tensor of dimension l^3t), and

$$\hat{\boldsymbol{\alpha}}(\omega)=-\frac{e^2}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\mathrm{Im}(\langle a\mid\mathbf{R}\mid j\rangle\langle j\mid\mathbf{R}\mid a\rangle)\;, \tag{14}$$

$$\boldsymbol{\kappa}(\omega)=\frac{e^2}{2cm\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\mid\mathbf{R}\mid j\rangle\langle j\mid\mathbf{L}\mid a\rangle)\;. \tag{15}$$

The magnetic dipole moment operator is

$$\begin{aligned}\mathbf{m}'&=-\frac{e}{2mc}\sum_{i=1}^{n}\mathbf{r}_i\times\left[\mathbf{p}_i+\frac{e}{c}\mathbf{A}(\mathbf{r}_i)\right]\\&=-\frac{e}{2mc}\sum_{i=1}^{n}\mathbf{r}_i\times\left[\mathbf{p}_i+\frac{e}{2c}\mathbf{B}\times\mathbf{r}_i\right]\\&=\mathbf{m}+\frac{e^2}{4mc^2}\sum_{i=1}^{n}[(\mathbf{r}_i\cdot\mathbf{B})\mathbf{r}_i-r_i^2\mathbf{B}]\;,\end{aligned} \tag{16}$$

whence we find, using (9) and (10), that the induced dipole moment is

$$\Delta\langle\mathbf{m}'\rangle=\mathbf{E}\cdot\boldsymbol{\kappa}+(\boldsymbol{\chi}^p+\boldsymbol{\chi}^d)\cdot\mathbf{B}-\dot{\mathbf{E}}\cdot\hat{\boldsymbol{\kappa}}+\hat{\boldsymbol{\chi}}^p\cdot\dot{\mathbf{B}}\;, \tag{17}$$

where

$$\boldsymbol{\chi}^p(\omega)=\frac{e^2}{4c^2m^2\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\mid\mathbf{L}\mid j\rangle\langle j\mid\mathbf{L}\mid a\rangle) \tag{18}$$

is the paramagnetic susceptibility in the angular momentum formalism, $\boldsymbol{\chi}^d$ is the diamagnetic contribution

$$\boldsymbol{\chi}^d=-\frac{e^2}{4mc^2}\left\langle a\left|\sum_{i=1}^{n}(r_i^2\mathbf{1}-\mathbf{r}_i\mathbf{r}_i)\right|a\right\rangle\;, \tag{19}$$

and where

$$\hat{\boldsymbol{\chi}}^p(\omega)=-\frac{e^2}{4c^2m^2\hbar}\times\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\mathrm{Im}(\langle a\mid\mathbf{L}\mid j\rangle\langle j\mid\mathbf{L}\mid a\rangle)\;. \tag{20}$$

In the absence of an external magnetic field the eigenstates to the unperturbed Hamiltonian may be chosen to be real (if $|a\rangle$ is degenerate): the antisymmetric tensors (14) and (20) and tensor (15) are identically vanishing. When a static magnetic field $\mathbf{B}_0$ is present, $|a\rangle, |j\rangle$ are the time-independent perturbed states and, as well as ω_{ja}, are functions of $\mathbf{B}_0$. In this case the effect of (14) and (15) is that of adding higher-order contributions to the induced moments. Introducing the operator representing the electric field of the electrons on nucleus I in (9),

$$\mathbf{E}_I^n=e\sum_{i=1}^{n}\frac{\mathbf{r}_i-\mathbf{R}_I}{|\mathbf{r}_i-\mathbf{R}_I|^3}=\mathbf{E}_{I0}^n\;, \tag{21}$$

the electronic contribution to the average electric field induced at the nucleus becomes

$$\Delta\langle\mathbf{E}_I^n\rangle=-\boldsymbol{\gamma}^I\cdot\mathbf{E}+\boldsymbol{\xi}^I\cdot\mathbf{B}-\hat{\boldsymbol{\gamma}}^I\cdot\dot{\mathbf{E}}+\hat{\boldsymbol{\xi}}^I\cdot\dot{\mathbf{B}}\;, \tag{22}$$

where

$$\boldsymbol{\gamma}^I(\omega)=\frac{e}{\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\mid\mathbf{E}_I^n\mid j\rangle\langle j\mid\mathbf{R}\mid a\rangle) \tag{23}$$

is the electric shielding of nucleus I (a dimensionless asymmetric tensor) in the length formalism. The tensor

$$\hat{\boldsymbol{\xi}}^I(\omega)=\frac{e}{2cm\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\mathrm{Im}(\langle a\mid\mathbf{E}_I^n\mid j\rangle\langle j\mid\mathbf{L}\mid a\rangle) \tag{24}$$

deserves to be called electromagnetic shielding (an axial tensor of dimension t). Its physical meaning is immediately gathered from (22): by taking the scalar dyadic product with the time derivative of the magnetic field, one obtains the electric field induced at the nucleus. In the absence of an external magnetic field, the tensors

$$\xi^I(\omega) = -\frac{e}{2cm\hbar} \sum_{j\,(\neq a)} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathrm{Re}(\langle a \,|\, \mathbf{E}_I^n \,|\, j \rangle \langle j \,|\, \mathbf{L} \,|\, a \rangle), \tag{25}$$

$$\hat{\gamma}^I(\omega) = -\frac{e}{\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^2 - \omega^2} \mathrm{Im}(\langle \,|\, \mathbf{E}_I^n \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, a \rangle) \tag{26}$$

are identically zero. Tensor (24) is related to a similar one introduced by Fowler and Buckingham.[16]

Using, in the notation of Ref. 11, the operator

$$\mathbf{B}_I^n = -\frac{e}{cm} \mathbf{M}_I^n \equiv \mathbf{B}_{I0}^n , \tag{27}$$

$$\mathbf{M}_I^n = \sum_{i=1}^{n} \frac{\mathbf{l}_i(\mathbf{R}_I)}{|\,\mathbf{r}_i - \mathbf{R}_I\,|^3} \tag{28}$$

the magnetic field operator is

$$\mathbf{B}_I^{n'} = \mathbf{B}_I^n + \frac{e}{2mc^2} \sum_{i=1}^{n} [(\mathbf{B}\cdot\mathbf{E}_I^i)\mathbf{r}_i - (\mathbf{E}_I^i \cdot \mathbf{r}_i)\mathbf{B}] \ . \tag{29}$$

and the expression for the magnetic field induced by the electrons at nucleus I is

$$\Delta\langle \mathbf{B}_I^{n'} \rangle = \boldsymbol{\lambda}^I \cdot \mathbf{E} - (\boldsymbol{\sigma}^{pI} + \boldsymbol{\sigma}^{dI}) \cdot \mathbf{B} + \hat{\boldsymbol{\lambda}}^I \cdot \dot{\mathbf{E}} - \hat{\boldsymbol{\sigma}}^{pI} \cdot \dot{\mathbf{B}} \ , \tag{30}$$

where the dimensionless quantity

$$\sigma^{pI}(\omega) = -\frac{e^2}{2c^2 m^2 \hbar} \sum_{j\,(\neq a)} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \times \mathrm{Re}(\langle a \,|\, \mathbf{M}_I^n \,|\, j \rangle \langle j \,|\, \mathbf{L} \,|\, a \rangle) \tag{31}$$

is the dynamic paramagnetic shielding tensor. Equation (31) is a generalization of Ramsey's definition[17] for the static property, and $\boldsymbol{\sigma}^{dI}$ is the diamagnetic shielding

$$\boldsymbol{\sigma}^{dI} = \frac{e^2}{2c^2 m} \left\langle a \,\middle|\, \sum_{i=1}^{n} (\mathbf{r}_i \cdot \mathbf{E}_I^i \mathbf{1} - \mathbf{r}_i \mathbf{E}_I^i) \,\middle|\, a \right\rangle \tag{32}$$

The diamagnetic terms (19) and (32) do not depend on the angular frequency ω. The axial tensor of dimension t,

$$\hat{\boldsymbol{\lambda}}^I(\omega) = -\frac{e^2}{cm\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^2 - \omega^2} \mathrm{Im}(\langle a \,|\, \mathbf{M}_I^n \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, a \rangle) \ , \tag{33}$$

may be called magnetoelectric shielding. The tensors

$$\boldsymbol{\lambda}^I(\omega) = \frac{e^2}{cm\hbar} \sum_{j\,(\neq a)} \frac{2\omega_{ja}}{\omega_{ja}^2 - \omega^2} \mathrm{Re}(\langle a \,|\, \mathbf{M}_I^n \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, a \rangle) \ , \tag{34}$$

$$\hat{\sigma}^{pI}(\omega) = \frac{e^2}{2c^2 m^2 \hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^2 - \omega^2} \times \mathrm{Im}(\langle a \,|\, \mathbf{M}_I^n \,|\, j \rangle \langle j \,|\, \mathbf{L} \,|\, a \rangle) \tag{35}$$

are identically vanishing in the absence of an external magnetic field. When an additional (static) magnetic field is present, then it will make contributions to (16) and (29), and (34) and (35) as was the case of (14) and (15), (20), and (25) and (26), yield higher-order contributions to the observable.

The tensors (23)–(26) and (33)–(35), introduced here possess interesting properties: we prove hereafter that they are interdependent and related to (12)–(15), (18), and (20).

The electric shielding satisfies the translational sum rule[1,2,4,5,8]

$$\sum_{I=1}^{N} Z_I \gamma^I(0) = n\mathbf{1} \ , \tag{36}$$

which is the Thomas-Reiche-Kuhn (TRK) relation written in the mixed length-acceleration formalism,[10] a condition for the conservation of the induced electronic current density, the hypervirial theorem[5] for the position operator (3), and a gauge-invariance constraint for the magnetic susceptibility.[11] Studying the conditions for translational gauge invariance of the magnetic properties, we have introduced the tensors[11]

$$(\mathbf{F}_n^N, \mathbf{R})_{-1} = -\frac{m}{\hbar} \sum_{j\,(\neq a)} 2\omega_{ja}^{-1} \mathrm{Re}(\langle a \,|\, \mathbf{F}_n^N \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, a \rangle) \ , \tag{37}$$

$$(\mathbf{K}_n^N, \mathbf{R})_{-1} = -\frac{m}{\hbar} \sum_{j\,(\neq a)} 2\omega_{ja}^{-1} \mathrm{Re}(\langle a \,|\, \mathbf{K}_n^N \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, a \rangle) \ , \tag{38}$$

$$(\mathbf{L}, \mathbf{F}_n^N)_{-2} = \frac{1}{\hbar} \sum_{j\,(\neq a)} 2\omega_{ja}^{-2} \mathrm{Im}(\langle a \,|\, \mathbf{L} \,|\, j \rangle \langle j \,|\, \mathbf{F}_n^N \,|\, a \rangle) \ , \tag{39}$$

involving the operators

$$\mathbf{F}_n^N = \sum_{I=1}^{N} \mathbf{F}_n^I = \sum_{i=1}^{n} \mathbf{F}_i^N, \quad \mathbf{F}_i^I = -e^2 Z_I \frac{\mathbf{r}_i - \mathbf{R}_I}{|\,\mathbf{r}_i - \mathbf{R}_I\,|^3} \ , \tag{40}$$

$$\mathbf{K}_n^N = \sum_{I=1}^{N} \mathbf{K}_n^I = \sum_{i=1}^{n} \mathbf{K}_i^N, \quad \mathbf{K}_i^I = e^2 Z_I \frac{\mathbf{r}_i - \mathbf{R}_I}{|\,\mathbf{r}_i - \mathbf{R}_I\,|^3} \times \mathbf{R}_I \ , \tag{41}$$

which represent, respectively, the force and the torque of the nuclei on the electrons, in the absence of external fields. From (37)–(41) one finds (sum over repeated greek indices)

$$\begin{aligned} \sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} (F_{n\gamma}^I, R_\delta)_{-1} &= (K_{n\alpha}^N, R_\delta)_{-1} = m \sum_{I=1}^{N} Z_I \epsilon_{\alpha\beta\gamma} R_{I\beta} \gamma^I(0)_{\gamma\delta} \\ &= m\epsilon_{\alpha\beta\delta} \langle R_\beta \rangle = (L_\alpha, F_{n\delta}^N)_{-2} = 2cm \sum_{I=1}^{N} Z_I \hat{\xi}^I(0)_{\delta\alpha} \ , \end{aligned} \tag{42}$$

which is identical to the gauge-invariance condition (71) of Ref. 11. This equation proves that the rotational sum rule[3,5,8,9(c)] for the electric shielding (third side) is the same as the translational rule for the electromagnetic shielding (sixth side), and, owing to the results of Ref. 11, it states the conservation of the current density field, the gauge invariance of magnetizability, and the fundamental operator commutation relations. This constitutes an interesting connection among electric and magnetic properties, and a general synthesis of various aspects. The relation between electric and electromagnetic shielding can be generalized for any ω

$$\sum_{I=1}^{N} Z_I \epsilon_{\alpha\beta\gamma} R_{I\beta} \gamma^I(\omega)_{\gamma\delta} = 2c \sum_{I=1}^{N} Z_I \hat{\xi}^I(\omega)_{\delta\alpha} . \tag{43}$$

The electric shieldings are also related to the polarizability.[2] Let us introduce the off-diagonal hypervirial relations

$$\begin{aligned}\langle a | \mathbf{R} | j \rangle &= \frac{i}{m} \omega_{ja}^{-1} \langle a | \mathbf{P} | j \rangle = -\frac{1}{m} \omega_{ja}^{-2} \langle a | \mathbf{F}_n^N | j \rangle \\ &= \frac{e}{m} \omega_{ja}^{-2} \sum_{I=1}^{N} Z_I \langle a | \mathbf{E}_I^n | j \rangle ,\end{aligned} \tag{44}$$

which amounts to choosing velocity and acceleration Hamiltonians, related to (1) via infinitesimal canonical transformations.[9]

Using (44) we rewrite the polarizability in the acceleration gauge

$$\boldsymbol{\alpha}(\omega) = \sum_{I=1}^{N} \boldsymbol{\alpha}^I(\omega) , \tag{45}$$

$$\boldsymbol{\alpha}^I(\omega) = \frac{e^3}{m\hbar} Z_I \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \mathrm{Re}(\langle a | \mathbf{E}_I^n | j \rangle \langle j | \mathbf{R} | a \rangle) . \tag{46}$$

Note that (46) is not symmetric and one could introduce the alternative definition

$$\tilde{\boldsymbol{\alpha}}^I(\omega) = \frac{e^3}{m\hbar} Z_I \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \mathrm{Re}(\langle a | \mathbf{R} | j \rangle \langle j | \mathbf{E}_I^n | a \rangle) . \tag{47}$$

From the identity

$$\frac{\omega_{ja}}{\omega_{ja}^2 - \omega^2} = \frac{1}{\omega_{ja}} + \frac{\omega^2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \tag{48}$$

one finds

$$\frac{e^2}{m} \omega^{-2} \sum_{I=1}^{N} Z_I [\boldsymbol{\gamma}^I(\omega) - \boldsymbol{\gamma}^I(0)] = \boldsymbol{\alpha}(\omega) . \tag{49}$$

Equation (49) is a resolution of the polarizability into atomic terms.[9] A partition of the electric shielding into atomic contributions[10] is also possible, allowing for the acceleration formalism

$$\boldsymbol{\gamma}^I(\omega) = \sum_{J=1}^{N} \boldsymbol{\gamma}^{IJ}(\omega) , \tag{50}$$

$$\boldsymbol{\gamma}^{IJ}(\omega) = \frac{e^2}{m\hbar} Z_J \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \mathrm{Re}(\langle a | \mathbf{E}_I^n | j \rangle \langle j | \mathbf{E}_J^n | a \rangle) , \tag{51}$$

$$Z_I \gamma_{\alpha\beta}^{IJ} = Z_J \gamma_{\beta\alpha}^{JI} . \tag{52}$$

Using (46) and (51) we find the resolution

$$\tilde{\boldsymbol{\alpha}}^I(\omega) = \frac{e^2}{m} \omega^{-2} \sum_{J=1}^{N} Z_J [\boldsymbol{\gamma}^{JI}(\omega) - \boldsymbol{\gamma}^{JI}(0)] . \tag{53}$$

A partition of the imaginary polarizability (14) analogous to (49) can be written in terms of imaginary electric shieldings (26) using the same procedure:

$$\hat{\boldsymbol{\alpha}}^I(\omega)_{\beta\alpha} = -\frac{e^2}{m} \omega^{-2} \sum_{J=1}^{N} Z_J [\hat{\gamma}^{JI}(\omega)_{\alpha\beta} - \hat{\gamma}^{JI}(0)_{\alpha\beta}] , \tag{53'}$$

$$\hat{\boldsymbol{\alpha}}(\omega) = \frac{e^2}{m} \omega^{-2} \sum_{I=1}^{N} Z_I [\hat{\boldsymbol{\gamma}}^I(\omega) - \hat{\boldsymbol{\gamma}}^I(0)] ; \tag{54}$$

note, however, that

$$\sum_{I=1}^{N} Z_I \hat{\boldsymbol{\gamma}}^I(0) = -\frac{2m}{\hbar} [\mathrm{Im}(\langle a | \mathbf{RR} | a \rangle) - \mathrm{Im}(\langle a | \mathbf{R} | a \rangle \langle a | \mathbf{R} | a \rangle)] = \mathbf{0} , \tag{55}$$

as the diagonal elements of Hermitian operators are real.

A rotational sum rule[16] for the electromagnetic shielding is also established introducing the tensor[11]

$$\begin{aligned}(\mathbf{K}_n^N, \mathbf{L})_{-2} &= -\frac{1}{\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^2} \mathrm{Im}(\langle a | \mathbf{K}_n^N | j \rangle \langle j | \mathbf{L} | a \rangle) \\ &= \frac{4m^2c^2}{e^2} \boldsymbol{\chi}^p(0) .\end{aligned} \tag{56}$$

Using (39) and (56) one finds

$$\begin{aligned}\sum_{I=1}^{N} Z_I \epsilon_{\alpha\beta\gamma} R_{I\beta} \hat{\xi}^I(0)_{\gamma\delta} &= \frac{1}{2cm} \sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} (F_{n\gamma}^I, L_\delta)_{-2} \\ &= \frac{1}{2cm} (K_{n\alpha}^N, L_\delta)_{-2} = \frac{2mc}{e^2} \chi^p(0)_{\alpha\delta} .\end{aligned} \tag{57}$$

This is another way of writing the same partition of the paramagnetic susceptibility into atomic Pascalian terms previously reported by us,[9]

$$\chi^{pI}(0)_{\alpha\delta} = \frac{e^2}{4m^2c^2} (K_{n\alpha}^I, L_\delta)_{-2} = \frac{e^2}{2mc} Z_I \epsilon_{\alpha\beta\gamma} R_{I\beta} \hat{\xi}^I(0)_{\gamma\delta} . \tag{57'}$$

The identity between the first and the last sides holds for any frequency, i.e.,

$$\sum_{I=1}^{N} Z_I \epsilon_{\alpha\beta\gamma} R_{I\beta} \hat{\xi}^{I}(\omega)_{\gamma\delta} = \frac{2mc}{e^2} \chi^{p}(\omega)_{\alpha\delta} . \tag{58}$$

In a similar way, introducing the tensors

$$(\mathbf{K}_n^N, \mathbf{F}_n^N)_{-3} = \frac{1}{\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^3} \mathrm{Re}(\langle a \mid \mathbf{K}_n^N \mid j \rangle \langle j \mid \mathbf{F}_n^N \mid a \rangle) , \tag{59}$$

$$(\mathbf{K}_n^N, \mathbf{K}_n^N)_{-3} = \frac{1}{\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^3} \mathrm{Re}(\langle a \mid \mathbf{K}_n^N \mid j \rangle \langle j \mid \mathbf{K}_n^N \mid a \rangle) , \tag{60}$$

we find again the static paramagnetic susceptibility in the torque formalism,[11]

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} R_{I\beta} (K_{n\delta}^N, F_{n\gamma}^I)_{-3} = (K_{n\delta}^N, K_{n\alpha}^N)_{-3} = \frac{4m^2c^2}{e^2} \chi^{p}(0)_{\delta\alpha} , \tag{57''}$$

which amounts to rewriting the rotational sum rule for the electromagnetic shielding in the acceleration-torque formalism.

We now show the explicit relation between the atomic contributions to (23) and (24). To this end let us introduce the hypervirial relation

$$\langle a \mid \mathbf{L} \mid j \rangle = i\omega_{ja}^{-1} \langle a \mid \mathbf{K}_n^N \mid j \rangle , \tag{61}$$

and the expression for the electromagnetic shielding within the acceleration-torque formalism[11]

$$\hat{\xi}^{I}(\omega) = \sum_{J=1}^{N} \hat{\xi}^{IJ}(\omega) , \tag{62}$$

$$\hat{\xi}^{IJ}(\omega) = -\frac{e}{2cm\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \mathrm{Re}(\langle a \mid \mathbf{E}_I^n \mid j \rangle \langle j \mid \mathbf{K}_n^J \mid a \rangle) . \tag{63}$$

Allowing for (51), one finds the equation relating electric and electromagnetic atomic shieldings

$$\epsilon_{\beta\gamma\delta} R_{J\gamma} \gamma^{IJ}(\omega)_{\alpha\beta} = -2c \hat{\xi}^{IJ}(\omega)_{\alpha\delta} , \tag{64}$$

$$\sum_{J=1}^{N} \epsilon_{\beta\gamma\delta} R_{J\gamma} \gamma^{IJ}(\omega)_{\alpha\beta} = -2c \hat{\xi}^{I}(\omega)_{\alpha\delta} . \tag{65}$$

An analogous relation exists between the polarizability (12) and the optical activity (13),

$$\epsilon_{\alpha\beta\gamma} \alpha^{I}(\omega)_{\beta\delta} R_{I\gamma} = 2c \hat{\kappa}^{I}(\omega)_{\delta\alpha} , \tag{66}$$

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} \alpha^{I}(\omega)_{\beta\delta} R_{I\gamma} = 2c \hat{\kappa}(\omega)_{\delta\alpha} , \tag{67}$$

where

$$\hat{\kappa}^{I}(\omega) = \frac{e^2}{2mc\hbar} \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}(\omega_{ja}^2 - \omega^2)} \times \mathrm{Re}(\langle a \mid \mathbf{R} \mid j \rangle \langle j \mid \mathbf{K}_n^I \mid a \rangle) \tag{68}$$

is an atomic optical activity within the length-torque gauge. Note that, using the alternative definition (47), one should rewrite

$$\sum_{I=1}^{N} \epsilon_{\alpha\beta\gamma} \tilde{\alpha}^{I}(\omega)_{\delta\beta} R_{I\gamma} = 2c \hat{\kappa}(\omega)_{\delta\alpha} . \tag{67'}$$

Owing to (49) we find a direct connection between the optical activity and the electric shielding

$$\frac{e^2}{2cm} \omega^{-2} \sum_{I=1}^{N} Z_I \epsilon_{\alpha\beta\gamma} R_{I\gamma} [\gamma^{I}(\omega)_{\beta\delta} - \gamma^{I}(0)_{\beta\delta}] = \hat{\kappa}(\omega)_{\delta\alpha} . \tag{67''}$$

A partition[16] of the optical activity in terms of the electromagnetic shielding is also easily proven via (43), or observing that

$$\frac{1}{\omega_{ja}^2 - \omega^2} = \frac{1}{\omega_{ja}^2} + \frac{\omega^2}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \tag{69}$$

and that the acceleration—angular-momentum version of the optical activity is

$$\hat{\kappa}(\omega) = \sum_{I=1}^{N} \hat{\kappa}^{I}(\omega) , \tag{70}$$

$$\hat{\kappa}^{I}(\omega) = -\frac{e^3}{2cm^2\hbar} Z_I \sum_{j\,(\neq a)} \frac{2}{\omega_{ja}^2(\omega_{ja}^2 - \omega^2)} \times \mathrm{Im}(\langle a \mid \mathbf{E}_I^n \mid j \rangle \langle j \mid \mathbf{L} \mid a \rangle) . \tag{71}$$

Hence

$$\hat{\kappa}(\omega) = -\frac{e^2}{m} \omega^{-2} \sum_{I=1}^{N} Z_I [\hat{\xi}^{I}(\omega) - \hat{\xi}^{I}(0)] . \tag{72}$$

A formally identical equation relates tensors (15) and (25). We find the rototranslational sum rules

$$\sum_{I=1}^{N} Z_I \xi^{I}(0) = \frac{1}{2mc} \langle a \mid P_\gamma \mid a \rangle \epsilon_{\alpha\beta\gamma} , \tag{73}$$

$$\sum_{I=1}^{N} Z_I \epsilon_{\alpha\beta\gamma} R_{I\beta} \xi^{I}(0)_{\gamma\delta} = \frac{1}{2cm} \epsilon_{\alpha\delta\gamma} \langle a \mid L_\gamma \mid a \rangle . \tag{74}$$

In the case of real functions, Eq. (73) satisfies the momentum theorem[5] trivially, and is identically vanishing (it is, in fact, a sum of zeros). In the presence of magnetic fields, however, the velocity theorem[5] holds, and (73) may be different from zero. Equations (66)—(72) are rather interesting, as they define an atomic additivity scheme for the optical activity of molecules. Since there is wide experimental evidence[18] that molecular polarizabilities can be written in terms of atomic contributions, transferable from molecule to molecule, our results would seem to imply that a similar partitioning is possible for the optical activity in terms of (67'') and (72). We observe, however, that the resolution (70) into atomic terms (71) is alternative to a corresponding one in terms of (68), as (68) and (71) define basically different quantities.

Relations analogous to (65) and (43) are

$$\epsilon_{\alpha\beta\gamma}\hat{\gamma}^{IJ}(\omega)_{\delta\beta}R_{J\gamma}=2c\omega^{-2}[\xi^{IJ}(\omega)_{\delta\alpha}-\xi^{IJ}(0)_{\delta\alpha}] , \tag{75}$$

$$\sum_{J=1}^{N}\epsilon_{\alpha\beta\gamma}\hat{\gamma}^{IJ}(\omega)_{\delta\beta}R_{J\gamma} =2c\omega^{-2}[\xi^{I}(\omega)_{\delta\alpha}-\xi^{I}(0)_{\delta\alpha}],\quad Z_I\hat{\gamma}^{IJ}_{\alpha\beta}=-Z_J\hat{\gamma}^{JI}_{\beta\alpha} ,$$

$$\sum_{I=1}^{N}\epsilon_{\alpha\beta\gamma}Z_I\hat{\gamma}^{I}(\omega)_{\beta\delta}R_{I\gamma}=-2c\omega^{-2}\sum_{I=1}^{N}Z_I[\xi^{I}(\omega)_{\delta\alpha}-\xi^{I}(0)_{\delta\alpha}] . \tag{76}$$

A large series of rotational sum rules can be obtained starting from tensors which involve the force operator.[11] For instance, from

$$(\mathbf{M}_I^n,\mathbf{F}_n^N)_{-2}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2}\mathrm{Im}(\langle a\,|\,\mathbf{M}_I^n\,|\,j\rangle\langle j\,|\,\mathbf{F}_n^N\,|\,a\rangle) , \tag{77}$$

one finds

$$\sum_{J=1}^{N}\epsilon_{\alpha\beta\gamma}R_{J\beta}(F_{n\gamma}^{J},M_{I\delta}^{n})_{-2} =(K_{n\alpha}^{N},M_{I\delta}^{n})_{-2}=-\frac{2m^2c^2}{e^2}\sigma^{pI}(0)_{\delta\alpha} . \tag{78}$$

Another interesting relation is found using the (F,F) formalism for the polarizability (12). We define "pair polarizabilities"

$$\alpha^{IJ}(\omega)=\frac{e^4}{m^2\hbar}Z_IZ_J\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^3(\omega_{ja}^2-\omega^2)} \times\mathrm{Re}(\langle a\,|\,\mathbf{E}_I^n\,|\,j\rangle\langle j\,|\,\mathbf{E}_J^n\,|\,a\rangle) , \tag{79}$$

such that $\boldsymbol{\alpha}(\omega)=\sum_{I,J=1}^{N}\boldsymbol{\alpha}^{IJ}(\omega)$. The $\boldsymbol{\alpha}^{II}$ are interpreted as "atomic" terms, whereas $\boldsymbol{\alpha}^{IJ}$ are "bond" polarizabilities. Using (60) we introduce "pair susceptibilities"

$$\chi^{pIJ}(\omega)=\frac{e^2}{4c^2m^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}(\omega_{ja}^2-\omega^2)} \times\mathrm{Re}(\langle a\,|\,\mathbf{K}_n^I\,|\,j\rangle\langle j\,|\,\mathbf{K}_n^J\,|\,a\rangle) ,$$

$$\chi^{pI}(\omega)=-\frac{e^2}{4c^2m^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2} \times\mathrm{Im}(\langle a\,|\,\mathbf{K}_n^I\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle) . \tag{80}$$

Allowing for the atomic contributions to the optical activity in the (F,L) formalism (71), we find

$$\epsilon_{\delta\gamma\alpha}\epsilon_{\lambda\mu\beta}R_{I\gamma}R_{J\mu}\alpha^{IJ}(\omega)_{\alpha\beta}=4c^2\omega^{-2}[\chi^{pIJ}(\omega)_{\delta\lambda}-\chi^{pIJ}(0)_{\delta\lambda}] ,$$

$$\epsilon_{\delta\gamma\alpha}R_{I\gamma}\hat{\kappa}^{I}(\omega)_{\alpha\lambda}=-2c\omega^{-2}[\chi^{pI}(\omega)_{\delta\lambda}-\chi^{pI}(0)_{\delta\lambda}] , \tag{81}$$

$$\sum_{I,J=1}^{N}\epsilon_{\delta\gamma\alpha}\epsilon_{\lambda\mu\beta}R_{I\gamma}R_{J\mu}\alpha^{IJ}(\omega)_{\alpha\beta}=-2c\sum_{I=1}^{N}\epsilon_{\delta\gamma\alpha}R_{I\gamma}\hat{\kappa}^{I}(\omega)_{\alpha\lambda} =4c^2\omega^{-2}[\chi^{p}(\omega)_{\delta\lambda}-\chi^{p}(0)_{\delta\lambda}],$$

which relates three different molecular properties. Magnetic and magnetoelectric shieldings can also be partitioned in terms of atomic contributions [see also (78)]

$$\hat{\sigma}^{pIJ}(\omega)=-\frac{e^2}{2c^2m^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}(\omega_{ja}^2-\omega^2)} \times\mathrm{Re}(\langle a\,|\,\mathbf{M}_I^n\,|\,j\rangle\langle j\,|\,\mathbf{K}_n^J\,|\,a\rangle) , \tag{82}$$

$$\sigma^{pIJ}(\omega)=-\frac{e^2}{2c^2m^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2)} \times\mathrm{Im}(\langle a\,|\,\mathbf{M}_I^n\,|\,j\rangle\langle j\,|\,\mathbf{K}_n^J\,|\,a\rangle) , \tag{83}$$

$$\lambda^{IJ}(\omega)=\frac{e^3}{cm^2\hbar}Z_J\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}(\omega_{ja}^2-\omega^2)} \times\mathrm{Re}(\langle a\,|\,\mathbf{M}_I^n\,|\,j\rangle\langle j\,|\,\mathbf{E}_J^n\,|\,a\rangle) , \tag{84}$$

$$\hat{\lambda}^{IJ}(\omega)=-\frac{e^3}{cm^2\hbar}Z_J\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2(\omega_{ja}^2-\omega^2)} \times\mathrm{Im}(\langle a\,|\,\mathbf{M}_I^n\,|\,j\rangle\langle j\,|\,\mathbf{E}_J^n\,|\,a\rangle) , \tag{85}$$

and a series of sum rules can be proven,

$$\epsilon_{\lambda\mu\delta}R_{J\mu}\hat{\lambda}^{IJ}(\omega)_{\gamma\delta}=-2c\omega^{-2}[\sigma^{pIJ}(\omega)_{\gamma\lambda}-\sigma^{pIJ}(0)_{\gamma\lambda}] , \tag{86}$$

$$\epsilon_{\lambda\mu\delta}R_{J\mu}\lambda^{IJ}(\omega)_{\gamma\delta}=-2c\hat{\sigma}^{pIJ}(\omega)_{\gamma\lambda} , \tag{86'}$$

$$\sum_{J=1}^{N}\epsilon_{\lambda\mu\delta}R_{J\mu}\hat{\lambda}^{IJ}(\omega)_{\gamma\delta} =-2c\omega^{-2}[\sigma^{pI}(\omega)_{\gamma\lambda}-\sigma^{pI}(0)_{\gamma\lambda}] , \tag{87}$$

$$\sum_{J=1}^{N}\epsilon_{\lambda\mu\delta}R_{J\mu}\lambda^{IJ}(\omega)_{\gamma\delta}=-2c\hat{\sigma}^{pI}(\omega)_{\gamma\lambda} . \tag{87'}$$

III. COMPLEX REPRESENTATION OF THE SHIELDING TENSORS

In some instances it is convenient to introduce a complex representation. This is particularly useful in order to account for absorption and stimulated emission.[15] The periodic fields (1) and (4) are the real part of

$$\mathbf{E}=\mathbf{E}_0\exp\left[i\omega\left[t-\frac{\mathbf{k}\cdot\mathbf{r}}{c}\right]\right],\quad \frac{\partial\mathbf{E}}{\partial t}=i\omega\mathbf{E} , \tag{88}$$

$$\mathbf{B}=\mathbf{B}_0\exp\left[i\omega\left[t-\frac{\mathbf{k}\cdot\mathbf{r}}{c}\right]\right]=\mathbf{k}\times\mathbf{E},\quad \frac{\partial\mathbf{B}}{\partial t}=i\omega\mathbf{B} . \tag{89}$$

To avoid cumbersome notation we adopt the conventions of Ref. 15: the new complex quantities $\mathbf{X}$ defined hereafter are equal to $\mathbf{X}+i\omega\hat{\mathbf{X}}$ defined in (11)–(18), (20), (23)–(26), and (30)–(36). The complex induced moments become

$$\Delta\langle \boldsymbol{\mu}\rangle = \boldsymbol{\alpha}\cdot\mathbf{E}+\boldsymbol{\kappa}\cdot\mathbf{B}\ , \tag{90}$$

$$\Delta\langle \mathbf{m}'\rangle = \mathbf{E}\cdot\boldsymbol{\kappa}^{*}+(\boldsymbol{\chi}^{p}+\boldsymbol{\chi}^{d})\cdot\mathbf{B}\ , \tag{91}$$

and the complex fields induced at the nuclei become

$$\Delta\langle \mathbf{E}_I^{n}\rangle = -\boldsymbol{\gamma}^{I}\cdot\mathbf{E}+\boldsymbol{\xi}^{I}\cdot\mathbf{B}\ , \tag{92}$$

$$\Delta\langle \mathbf{B}_I^{n'}\rangle = \boldsymbol{\lambda}^{I}\cdot\mathbf{E}-(\boldsymbol{\sigma}^{pI}+\boldsymbol{\sigma}^{dI})\cdot\mathbf{B}\ . \tag{93}$$

The complex tensors are defined

$$\boldsymbol{\alpha}(\omega)=\frac{e^2}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{R}\,|\,j\rangle\langle j\,|\,\mathbf{R}\,|\,a\rangle)-i\omega\,\mathrm{Im}(\langle a\,|\,\mathbf{R}\,|\,j\rangle\langle j\,|\,\mathbf{R}\,|\,a\rangle)]=\boldsymbol{\alpha}^{\dagger}\ , \tag{94}$$

$$\boldsymbol{\kappa}(\omega)=\frac{e^2}{2cm\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{R}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)-i\omega\,\mathrm{Im}(\langle a\,|\,\mathbf{R}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)]\ , \tag{95}$$

$$\boldsymbol{\chi}^{p}(\omega)=\frac{e^2}{4c^2m^2\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{L}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)-i\omega\,\mathrm{Im}(\langle a\,|\,\mathbf{L}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)]=\boldsymbol{\chi}^{p\dagger}\ , \tag{96}$$

$$\boldsymbol{\gamma}^{I}(\omega)=\frac{e}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{E}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{R}\,|\,a\rangle)-i\omega\,\mathrm{Im}(\langle a\,|\,\mathbf{E}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{R}\,|\,a\rangle)]\ , \tag{97}$$

$$\boldsymbol{\xi}^{I}(\omega)=-\frac{e}{2cm\hbar}\sum_{j(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{E}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)-i\omega\mathrm{Im}(\langle a\,|\,\mathbf{E}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)]\ , \tag{98}$$

$$\boldsymbol{\sigma}^{pI}(\omega)=-\frac{e^2}{2c^2m^2\hbar}\sum_{j(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{M}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)-i\omega\,\mathrm{Im}(\langle a\,|\,\mathbf{M}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{L}\,|\,a\rangle)]\ , \tag{99}$$

$$\boldsymbol{\lambda}^{I}(\omega)=\frac{e^2}{cm\hbar}\sum_{j(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}[\omega_{ja}\mathrm{Re}(\langle a\,|\,\mathbf{M}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{R}\,|\,a\rangle)-i\omega\,\mathrm{Im}(\langle a\,|\,\mathbf{M}_I^{n}\,|\,j\rangle\langle j\,|\,\mathbf{R}\,|\,a\rangle)]\ . \tag{100}$$

The actual moments are the real parts of (90) and (91) and the real fields are the real parts of (92) and (93).

IV. THE EFFECT OF ELECTRIC FIELD GRADIENT

In the case of small wavelengths the dipole approximation cannot be justified, as the electric field gradient $\mathbf{F}$ over the molecular dimensions becomes appreciable. In fact, the electric quadrupole terms are of the same order as the magnetic dipole, and should be included in the electronic Hamiltonians (1)–(6), adding the term

$$H^{\mathrm{F}}=-\tfrac{1}{3}\Theta_{\alpha\beta}F_{\alpha\beta},\quad F_{\alpha\beta}=\nabla_\alpha E_\beta\ , \tag{101}$$

$$\Theta=-\tfrac{1}{2}e\sum_{i=1}^{n}(3\mathbf{r}_i\mathbf{r}_i-r_i^2\mathbf{1})\ . \tag{102}$$

Accordingly, from propagator theory,[12] the term

$$\Delta\langle T\rangle_a=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\left[\omega_{ja}\mathrm{Re}(\langle a\,|\,T_0\,|\,j\rangle\langle j\,|\,H^{\mathrm{F}}\,|\,a\rangle)-\mathrm{Im}\left[\langle a\,|\,T_0\,|\,j\rangle\left\langle j\left|\frac{\partial H^{\mathrm{F}}}{\partial t}\right|a\right\rangle\right]\right] \tag{103}$$

must be added to (9). In the case of the induced electric and magnetic dipole moments one finds[15]

$$\Delta\langle \mu_\alpha\rangle=\tfrac{1}{3}A_{\alpha,\beta\gamma}F_{\beta\gamma}+\tfrac{1}{3}\hat{A}_{\alpha,\beta\gamma}\dot{F}_{\beta\gamma}\ , \tag{104}$$

$$\Delta\langle m'_\alpha\rangle=\tfrac{1}{3}D_{\alpha,\beta\gamma}F_{\beta\gamma}+\tfrac{1}{3}\hat{D}_{\alpha,\beta\gamma}\dot{F}_{\beta\gamma}\ , \tag{105}$$

where

$$A(\omega)_{\alpha,\beta\gamma}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\,|\,\mu_\alpha\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\ , \tag{106}$$

$$\hat{A}(\omega)_{\alpha,\beta\gamma}=-\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\times\mathrm{Im}(\langle a\,|\,\mu_\alpha\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\ , \tag{107}$$

$$D(\omega)_{\alpha,\beta\gamma}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\,|\,m_\alpha\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\,, \tag{108}$$

$$\hat{D}(\omega)_{\alpha,\beta\gamma}=-\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\times\mathrm{Im}(\langle a\,|\,m_\alpha\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\,. \tag{109}$$

In the case of the electron contribution to the electric and magnetic fields induced at nucleus I, one should add the terms

$$\Delta\langle E_{I\alpha}^{n}\rangle=\tfrac{1}{3}\nu_{\alpha,\beta\gamma}^{I}F_{\beta\gamma}+\tfrac{1}{3}\hat{\nu}_{\alpha,\beta\gamma}^{I}\dot{F}_{\beta\gamma}\,, \tag{110}$$

$$\Delta\langle B_{I\alpha}^{n'}\rangle=\tfrac{1}{3}\tau_{\alpha,\beta\gamma}^{I}F_{\beta\gamma}+\tfrac{1}{3}\hat{\tau}_{\alpha,\beta\gamma}^{I}\dot{F}_{\beta\gamma}\,, \tag{111}$$

where

$$\nu^{I}(\omega)_{\alpha,\beta\gamma}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\mathrm{Re}(\langle a\,|\,E_{I\alpha}^{n}\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle) \tag{112}$$

has been previously introduced by Fowler and Buckingham,[8] and the other tensors are defined

$$\hat{\nu}^{I}(\omega)_{\alpha,\beta\gamma}=-\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\times\mathrm{Im}(\langle a\,|\,E_{I\alpha}^{n}\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\,, \tag{113}$$

$$\tau^{I}(\omega)_{\alpha,\beta\gamma}=\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\times\mathrm{Re}(\langle a\,|\,B_{I\alpha}^{n}\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\,, \tag{114}$$

$$\hat{\tau}^{I}(\omega)_{\alpha,\beta\gamma}=-\frac{1}{\hbar}\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}^2-\omega^2}\times\mathrm{Im}(\langle a\,|\,B_{I\alpha}^{n}\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\,. \tag{115}$$

Rewriting the mixed dipole-quadrupole polarizability in the acceleration formalism,

$$A(\omega)_{\alpha\beta,\gamma}=-\frac{e^2}{m\hbar}\sum_{I=1}^{N}Z_I\sum_{j\,(\neq a)}\frac{2}{\omega_{ja}(\omega_{ja}^2-\omega^2)}\times\mathrm{Re}(\langle a\,|\,E_{I\alpha}^{n}\,|\,j\rangle\langle j\,|\,\Theta_{\beta\gamma}\,|\,a\rangle)\,, \tag{116}$$

one finds the resolution into atomic terms[8]

$$\mathbf{A}(\omega)=-\frac{e^2}{m}\omega^{-2}\sum_{I=1}^{N}Z_I[\boldsymbol{\nu}^{I}(\omega)-\boldsymbol{\nu}^{I}(0)]\,. \tag{117}$$

The translational and rotational sum rules for the mixed dipole-quadrupole shielding are[8]

$$\sum_{I=1}^{N}Z_I\nu^{I}(0)_{\alpha,\beta\gamma}=\langle R_\alpha\rangle\delta_{\beta\gamma}-\tfrac{3}{2}\langle R_\beta\rangle\delta_{\alpha\gamma}-\tfrac{3}{2}\langle R_\gamma\rangle\delta_{\alpha\beta}\,, \tag{118}$$

$$\sum_{I=1}^{N}Z_I\epsilon_{\alpha\beta\gamma}R_{I\beta}\nu^{I}(0)_{\gamma,\epsilon\delta}=\frac{1}{e}(\langle\Theta_{\beta\delta}\rangle\epsilon_{\alpha\beta\epsilon}+\langle\Theta_{\beta\epsilon}\rangle\epsilon_{\alpha\beta\delta})\,. \tag{119}$$

We obtain corresponding relations for tensor (113):

$$\sum_{I=1}^{N}Z_I\hat{\nu}^{I}(0)_{\alpha,\beta\gamma}=0\,, \tag{118$'$}$$

$$\sum_{I=1}^{N}Z_I\epsilon_{\alpha\beta\gamma}R_{I\beta}\hat{\nu}^{I}(\omega)_{\gamma,\epsilon\delta}=\frac{2cm}{e^2}D(\omega)_{\alpha,\epsilon\delta}\,. \tag{119$'$}$$

One can also define atomic contributions to (109) via the equation

$$\hat{D}(\omega)_{\alpha,\delta\epsilon}=-\frac{e^2}{2mc}\omega^{-2}\sum_{I=1}^{N}Z_I\epsilon_{\alpha\beta\gamma}R_{I\beta}[\nu^{I}(\omega)_{\gamma,\delta\epsilon}-\nu^{I}(0)_{\gamma,\delta\epsilon}]=\frac{1}{2c}\sum_{I=1}^{N}\epsilon_{\alpha\beta\gamma}R_{I\beta}A^{I}(\omega)_{\gamma,\delta\epsilon}\,. \tag{120}$$

In the absence of an external magnetic field the wave functions may be chosen real and (107), (108), (113), and (114) are identically zero. Eventually we observe that the tensors examined in this section can be given a complex representation introducing the complex gradient

$$F_{\alpha\beta}=-\frac{i\omega k_\alpha}{c}E_{0\beta}\exp\left[i\omega\left[t-\frac{\mathbf{k}\cdot\mathbf{r}}{c}\right]\right]\,. \tag{121}$$

V. CALCULATIONS ON THE WATER MOLECULE

As a first numerical application of the theory presented here, we report the results of an accurate calculation on the water molecule. The general propagator equations of linear-response theory[12] were solved allowing for the RPA,[19] according to a computational scheme previously described by us.[2,11] The ground-state reference wave function is a near-Hartree-Fock determinant. The molecular orbitals are expanded over a set of 101 uncontracted Gaussians, which yielded very accurate theoretical estimates of nuclear electric shieldings and dipole polarizability.[10]

A first idea of the high quality of the present calculation is grasped from the results of Table I, which reports the sum rules (42) written in several formalisms. Equation (42) should be exactly fulfilled in the limit of a complete basis set: our calculations show that (42) is fairly well satisfied. The results deteriorate only when force and torque operators are considered: this is expected on the basis of Dalgarno-Epstein conditions,[20] as the Cartesian Gaussians are not suitable to mimic the r^{-3} dependencies of these operators.[11] At any rate, we recall that (42) holds exactly allowing for the proper formalisms. For instance, as can be checked in Table I,

$$(L_y,F_{nx}^N)_{-2}=2c\sum_{I=1}^{N} Z_I\xi_L^I(0)_{xy}=-0.15092\ , \tag{122}$$

$$(K_{ny}^N,F_{nx}^N)_{-3}=2c\sum_{I=1}^{N} Z_I\xi_K^I(0)_{xy}=\sum_{I=1}^{N} Z_I\epsilon_{y\beta\gamma}R_{I\beta}\gamma_F^I(0)_{\gamma x}=-0.14582\ , \tag{123}$$

$$(K_{ny}^N,R_x)_{-2}=\sum_{I=1}^{N} Z_I\epsilon_{y\beta\gamma}R_{I\beta}\gamma_R^I(0)_{\gamma x}=-0.18056\ , \tag{124}$$

where the electromagnetic shielding is written in the angular momentum (L) and torque (K) gauges, and the electric shielding is expressed in the force (F) and length (R) gauges.

Similar conclusions can be drawn from the results in Table II, where the sum rules[11] for the gauge invariance of the magnetic shielding are reported: the results are good, with the exception of $(M_{\mathrm{O}x}^n,F_{ny}^N)_{-2}$, which is of wrong sign. A similar drawback was observed in the case of the HF molecule:[11] such a failure indicates deficiencies of our wave function in the environment of the heavy atom, related to the inadequacy of Gaussians in representing the torque operator.[20]

The equation for the theoretical average magnetic susceptibility, as a function of the distance from the origin of the gauge (the molecular center of mass), is (in a.u.)

$$\Delta\chi(r)_{\mathrm{av}}=-0.21629z-0.12021x^2-0.74574y^2-0.59775z^2\ . \tag{125}$$

TABLE I. Sum rules $[\langle z\rangle=(R_x,L_y)_0=\cdots-(F_{ny}^N,K_{nx}^N)_{-3}=2c\sum_{I=1}^{N}Z_I\hat{\xi}^I(0)_{xy}=\sum_{I=1}^{N}Z_I\epsilon_{y\beta\gamma}R_{I\beta}\gamma^I(0)_{\gamma x}]$ (42) and quantities necessary to evaluate the magnetic susceptibility for any gauge. RPA results in atomic units (a.u.); gauge origin is molecular center of mass (c.m.); atomic coordinates are (0,0,0.124 144 4) for O, (0, + 1.431 530 0, − 0.985 265 6) for H(1) and (0, − 1.431 530 0, − 0.985 265 6) for H(2).

$\langle z\rangle$	−0.196 95
$(L_y,R_x)_0$	−0.185 64
$(L_x,R_y)_0$	0.189 70
$(L_y,P_x)_{-1}$	−0.181 35
$(L_x,P_y)_{-1}$	0.188 18
$(K_{ny}^N,R_x)_{-1}$	−0.180 56
$(K_{nx}^N,R_y)_{-1}$	0.189 03
$(K_{ny}^N,P_x)_{-2}$	−0.176 89
$(K_{nx}^N,P_y)_{-2}$	0.187 91
$(L_y,F_{nx}^N)_{-2}$	−0.150 92
$(L_x,F_{ny}^N)_{-2}$	0.156 54
$(K_{ny}^N,F_{nx}^N)_{-3}$	−0.145 82
$(K_{nx}^N,F_{ny}^N)_{-3}$	0.156 70

TABLE II. Sum rules $[\langle E_{Iz}^n\rangle=(R_x,M_{Iy}^n)_0=-(R_y,M_{Ix}^n)_0$, $\langle E_{Iy}^n\rangle=(R_z,M_{Ix}^n)_0=-(R_x,M_{Iz}^n)_0]$ and quantities necessary to evaluate the static nuclear magnetic shielding for any gauge. RPA results in a.u.; gauge origin is molecular center of mass.

$\langle E_{\mathrm{O}z}^n\rangle$	−0.373 27		
$(M_{\mathrm{O}x}^n,R_y)_0$	0.356 61		
$(M_{\mathrm{O}y}^n,R_x)_0$	−0.354 76		
$(M_{\mathrm{O}x}^n,P_y)_{-1}$	0.359 70		
$(M_{\mathrm{O}y}^n,P_x)_{-1}$	−0.377 29		
$(M_{\mathrm{O}x}^n,F_{ny}^N)_{-2}$	−0.008 63		
$(M_{\mathrm{O}y}^n,F_{nx}^N)_{-2}$	0.192 34		
$\langle E_{\mathrm{H}(1)z}^n\rangle$	1.501 22	$\langle E_{\mathrm{H}(1)y}^n\rangle$	−2.055 39
$(M_{\mathrm{H}(1)x}^n,R_y)_0$	−1.484 63	$(M_{\mathrm{H}(1)x}^n,R_z)_0$	−2.008 78
$(M_{\mathrm{H}(1)y}^n,R_x)_0$	1.475 84	$(M_{\mathrm{H}(1)z}^n,R_x)_0$	2.011 99
$(M_{\mathrm{H}(1)x}^n,P_y)_{-1}$	−1.486 15	$(M_{\mathrm{H}(1)x}^n,P_z)_{-1}$	−2.003 11
$(M_{\mathrm{H}(1)y}^n,P_x)_{-1}$	1.458 82	$(M_{\mathrm{H}(1)z}^n,P_x)_{-1}$	1.990 71
$(M_{\mathrm{H}(1)x}^n,F_{ny}^N)_{-2}$	−1.465 92	$(M_{\mathrm{H}(1)x}^n,F_{nz}^N)_{-2}$	−1.982 55
$(M_{\mathrm{H}(1)y}^n,F_{nx}^N)_{-2}$	1.450 51	$(M_{\mathrm{H}(1)z}^n,F_{nx}^N)_{-2}$	1.959 00

This result is the best we obtained so far,[21] and indicates a very high degree of gauge independence. Moccia's[26] "best gauge" origin is obtained by extremizing (125): it lies on the **z** axis, −0.180 92 bohr from the center of mass. The paramagnetic susceptibilities in Table III are expected to be virtually coincident with the Hartree-Fock limit:[21] we think that the computed values obtained here are comparable with, or superior to, other theoretical predictions.[21] In any event the agreement with the experimental data is fairly good, as can be observed in Table III.

Inspection of Tables IV and V leads to similar conclusions as regards the magnetic shielding of oxygen and hydrogen. The results are characterized by a large degree of gauge independence and are in excellent agreement with the experimental values.[22–24] We can argue that the present theoretical predictions are to be classified among the most accurate reported so far.[25]

A partition of the paramagnetic shielding at $\omega=0$ and 0.3 a.u. is presented in Table VI and VII. These values can be used to check sum rules (78), (86), and (87).

A definite conclusion about the accuracy of the theoretical electromagnetic and magnetoelectric shieldings reported in Tables VIII–XI is not possible. However, the different formalisms give, in general, very similar numerical response, which could imply accuracy of the calculation.

The optical activity tensor in parts per thousand (ppt) is reported in Table XII. Of course, optical activity, which is related to the trace of this tensor, is uniquely observed in molecules possessing only proper rotations as symmetry elements. Accordingly, it is identically zero in water. The only nonvanishing components are $\hat{\kappa}_{xy},\hat{\kappa}_{yx}$. No comparison with corresponding experimental values is possible. In any event, we observe that the results obtained within different formalism are very close to each other, indicating good reliability of the calculation. We verify on this table that the atomic terms (68) and (71) are, in fact, different. We also found that the sum rules (43), (57), (67″), and (72) are obeyed to a very good extent, which provides a further criterion for relative accuracy of

TABLE III. RPA static magnetic susceptibility in ppm a.u. The entries within parentheses specify the gauge origin: c.m. stands for the molecular center of mass, BG for the best gauge origin (see text).

	χ^p_{LL} (c.m.)	χ^p_{LK} (c.m.)	χ^p_{KK} (c.m.)	χ^d (c.m.)	χ_{LL} (c.m.)	χ^p_{LL} (BG)	χ^d (BG)	χ_{LL} (BG)
xx	26.473	26.019	25.608	−183.360	−156.887	30.284	−187.125	−156.841
	26.79±0.52[a]							
	26.1[b]							
yy	7.485	7.465	7.462	−161.983	−154.498	11.263	−165.748	−154.485
	8.74±0.02[a]							
	8.9[b]							
zz	14.166	14.003	13.872	−171.435	−157.269	14.166	−171.435	−157.269
	15.17±0.38[a]							
	15.7[b]							
Avg.	16.042	15.829	15.647	−172.259	−156.217	18.571	−174.769	−156.198
	16.90[a]							
	16.9[b]							

[a]Experimental values from Refs. 22 and 23.
[b]Experimental values from Ref. 24.

TABLE IV. Magnetic shielding at ^{17}O in ppm; entries within parentheses specify the gauge origin.

	σ^d (c.m.)	σ^p (c.m.)	σ (c.m.)	σ^d (O)	σ^p (O)	σ (O)
xx	415.870	−111.806	304.064	417.104	−112.995	304.109
yy	413.970	−48.613	365.357	415.204	−49.860	365.344
zz	415.740	−103.779	311.961	415.740	−103.779	311.961
Avg.	415.193	−88.066	327.127	416.016	−88.878	327.138
Expt.[a]			334±15			

[a]Value taken from Ref. 25.

TABLE V. Magnetic shielding at ^1H in ppm; entries within parentheses specify the gauge origin.

	σ^d (c.m.)	σ^p (c.m.)	σ (c.m.)	σ^d [H(1)]	σ^p [H(1)]	σ [H(1)]
xx	12.660	9.359	22.019	130.384	−105.977	24.407
		9.2[a]			−107.04[a]	
yy	36.365	1.877	38.242	75.747	−36.394	39.353
		1.5[a]			−36.57[a]	
zz	22.711	6.670	29.381	101.053	−69.207	31.846
		7.4[a]			−71.79[a]	
yz	−17.994	7.650	−10.344	39.226	−47.955	−8.729
zy	−14.694	5.685	−9.009	39.226	−46.538	−7.312
Avg.	23.912	5.968	29.880	102.395	−70.526	31.869
			30.2[a]	102.4[a]	−71.80[a]	30.2[a]

[a]Experimental values from Refs. 21 and 25.

TABLE VI. Partition of paramagnetic shielding tensor at $\omega=0$, in ppm; gauge origin is c.m.

Atomic Contributions I	J	Formalism	σ^{pI}_{xx}	σ^{pI}_{yy}	σ^{pI}_{zy}	σ^{pI}_{yz}	σ^{pI}_{zz}
O		(M_O,L)	−111.806	−48.613	0.0	0.0	−103.779
O	O		−4.734	−6.133	0.0	0.0	0.0
O	H(1)		−53.305	−21.815	−35.235	−31.695	−51.194
O	H(2)		−53.305	−21.815	35.235	31.695	−51.194
O		(M_O,K)	−111.344	−49.762	0.0	0.0	−102.388
H(1)		(M_H,L)	9.359	1.877	5.685	7.650	6.670
H(1)	O		−4.068	−4.036	−5.098	0.0	0.0
H(1)	H(1)		15.057	5.660	7.815	8.224	11.354
H(1)	H(2)		−1.528	0.362	3.116	−0.526	−4.527
H(1)		(M_H,K)	9.461	1.987	5.832	7.698	6.827

TABLE VII. Partition of paramagnetic shielding tensor at $\omega=0.3$ a.u., in ppm; gauge origin is c.m.

Atomic Contributions I	J	Formalism	σ^{pI}_{xx}	σ^{pI}_{yy}	σ^{pI}_{zy}	σ^{pI}_{yz}	σ^{pI}_{zz}
O		(M_O,L)	−169.064	−421.457	0.0	0.0	−225.955
O	O		−7.764	−7.625	0.0	0.0	0.0
O	H(1)		−80.324	−212.612	−76.628	−308.912	−111.336
O	H(2)		−80.324	−212.612	76.628	308.912	−111.336
O		(M_O,K)	−168.411	−432.849	0.0	0.0	−222.672
H(1)		(M_H,L)	11.257	8.436	25.817	11.496	8.407
H(1)	O		−4.166	−4.271	−5.340	0.0	0.0
H(1)	H(1)		17.012	10.459	18.873	15.197	27.421
H(1)	H(2)		−1.495	2.554	12.992	−3.710	−18.876
H(1)		(M_H,K)	11.352	8.436	26.524	11.487	8.545

TABLE VIII. Electromagnetic shielding tensor at $\omega=0$, in ppt a.u.; gauge origin is c.m.

Atomic Contributions I	J	Formalism	$\hat{\xi}^I_{xy}$	$\hat{\xi}^I_{yx}$	$\hat{\xi}^I_{xz}$	$\hat{\xi}^I_{zx}$
O		(F,L)	0.169	−0.219	0.0	0.0
O	O		0.450	−0.469	0.0	0.0
O	H(1)		−0.139	0.126	−0.203	0.292
O	H(2)		−0.139	0.126	0.203	−0.292
O		(F,K)	0.171	−0.217	0.0	0.0
H(1)		(F,L)	−0.953	1.161	−1.340	1.616
H(1)	O		0.141	−0.043	0.0	−0.058
H(1)	H(1)		−1.003	0.766	−1.457	1.540
H(1)	H(2)		−0.089	0.430	0.129	0.101
H(1)		(F,K)	−0.951	1.153	−1.328	1.583

TABLE IX. Electromagnetic shielding tensor at $\omega=0.3$, in ppt a.u.; gauge origin is c.m.

Atomic Contributions I	J	Formalism	$\hat{\xi}^I_{xy}$	$\hat{\xi}^I_{yx}$	$\hat{\xi}^I_{xz}$	$\hat{\xi}^I_{zx}$
O		(F,L)	0.169	−0.268	0.0	0.0
O	O		0.485	−0.502	0.0	0.0
O	H(1)		−0.157	0.119	−0.223	0.326
O	H(2)		−0.157	0.119	0.223	−0.326
O		(F,K)	0.170	−0.265	0.0	0.0
H(1)		(F,L)	−2.273	1.319	−1.727	1.935
H(1)	O		0.159	−0.047	0.0	−0.050
H(1)	H(1)		−1.822	0.758	−2.647	1.858
H(1)	H(2)		−0.644	0.601	0.936	0.088
H(1)		(F,K)	−2.307	1.311	−1.711	1.896

TABLE X. Magnetoelectric shielding tensor at $\omega=0$, in ppt a.u.

Atomic Contributions I	J	Formalism	$\hat{\lambda}^I_{xy}$	$\hat{\lambda}^I_{yx}$	$\hat{\lambda}^I_{xz}$	$\hat{\lambda}^I_{zx}$
O		(M_O,R)	−28.560	−83.352	0.0	0.0
O		(M_O,P)	−28.642	−83.049	0.0	0.0
O	O		−55.277	73.287	0.0	0.0
O	H(1)		8.819	−61.861	31.676	−56.065
O	H(2)		8.819	−61.861	−31.676	56.065
O		(M_O,F)	−37.640	−50.434	0.0	0.0
H(1)		(M_H,R)	−5.581	7.040	−10.622	12.457
H(1)		(M_H,P)	−5.584	7.041	−10.627	12.420
H(1)	O		−2.310	3.491	−4.362	1.999
H(1)	H(1)		0.824	3.403	−3.442	5.238
H(1)	H(2)		−3.799	−0.400	−2.397	3.419
H(1)		(M_O,F)	−5.285	6.494	−10.201	10.656

TABLE XI. Magnetoelectric shielding tensor at $\omega=0.3$, in ppt a.u.

Atomic Contributions I	J	Formalism	$\hat{\lambda}^I_{xy}$	$\hat{\lambda}^I_{yx}$	$\hat{\lambda}^I_{xz}$	$\hat{\lambda}^I_{zx}$
O		(M_O,R)	−50.119	−1412.279	0.0	0.0
O		(M_O,P)	−50.276	−1428.767	0.0	0.0
O	O		−74.315	36.597	0.0	0.0
O	H(1)		5.299	−589.714	53.829	−127.938
O	H(2)		5.299	−589.714	−53.829	127.938
O		(M_O,F)	−63.717	−1142.831	0.0	0.0
H(1)		(M_H,R)	−6.577	32.025	−17.317	84.837
H(1)		(M_H,P)	−6.581	32.368	−17.333	85.755
H(1)	O		−2.388	5.783	−5.293	5.942
H(1)	H(1)		3.260	14.833	−6.402	34.177
H(1)	H(2)		−7.018	6.774	−4.759	30.525
H(1)		(M_H,F)	−6.147	27.390	−16.454	70.643

TABLE XII. Optical activity tensor at $\omega=0$ and 0.3, in ppt a.u.; gauge origin is c.m.

Atomic Contributions	Formalism	$\hat{\kappa}(0)_{xy}$	$\hat{\kappa}(0)_{yx}$	$\hat{\kappa}(0.3)_{xy}$	$\hat{\kappa}(0.3)_{yx}$
	(R,L)	4.466	−0.295	35.483	0.386
	(P,L)	4.470	−0.313	35.904	0.363
O	(R,K^O)	−2.531	2.522	−3.544	3.039
H(1)[H(2)]	(R,K^H)	3.559	−1.447	20.042	−1.386
Total	(R,K)	4.588	−0.373	36.541	0.267
O	(P,K^O)	−2.524	2.525	−3.553	3.044
H(1)[H(2)]	(P,K^H)	3.560	−1.458	20.266	−1.400
Total	(P,K)	4.595	−0.391	36.979	0.244
O	(F,K^O)	−2.528	2.534	−3.495	3.057
H(1)[H(2)]	(F,K^H)	3.155	−1.290	16.863	−1.161
Total	(F,K)	3.782	−0.046	30.232	0.736
O	(F^O,L)	−1.176	3.061	0.020	4.358
H(1)[H(2)]	(F^H,L)	2.427	−1.513	14.664	−1.750
Total	(F,L)	3.679	0.035	29.348	0.857
O	(F^O,K)	−1.163	2.993	0.106	4.263
H(1)[H(2)]	(F^H,K)	2.472	−1.520	15.063	−1.764
Total	(F,K)	3.782	−0.046	30.232	0.736

TABLE XIII. Partition of paramagnetic susceptibility at $\omega=0$, in ppm a.u.; gauge origin is c.m.

Atomic Contributions I	J	Formalism	χ^p_{xx}	χ^p_{yy}	χ^p_{yz}	χ^p_{zy}	χ^p_{zz}
		(L,L)	26.473	7.485	0.0	0.0	14.166
O			0.793	0.614	0.0	0.0	0.0
H(1)			12.613	3.426	4.819	4.977	7.001
H(2)			12.613	3.426	−4.819	−4.977	7.001
Total		(K,L)	26.019	7.465	0.0	0.0	14.003
O	O		1.698	1.632	0.0	0.0	0.0
O	H(1)		−0.456	−0.505	−0.734	0.0	0.0
O	H(2)		−0.456	−0.505	0.734	0.0	0.0
H(1)	H(1)		10.795	3.606	5.239	5.239	7.612
H(1)	H(2)		2.073	0.320	−0.465	0.465	−0.676
O			0.785	0.621	0.0	0.0	0.0
H(1)			12.411	3.420	4.774	4.970	6.936
H(2)			12.411	3.420	−4.774	−4.970	6.936
Total		(K,K)	25.608	7.462	0.0	0.0	13.872

TABLE XIV. Partition of paramagnetic susceptibility at $\omega=0.3$, in ppm a.u.; gauge origin is c.m.

Atomic Contributions I	J	Formalism	χ^p_{xx}	χ^p_{yy}	χ^p_{yz}	χ^p_{zy}	χ^p_{zz}
		(L,L)	31.172	16.727	0.0	0.0	18.244
O			0.971	0.613	0.0	0.0	0.0
H(1)			14.846	8.170	6.208	11.870	9.020
H(2)			14.846	8.170	−6.208	−11.870	9.020
Total		(K,L)	30.663	16.953	0.0	0.0	18.040
O	O		1.818	1.758	0.0	0.0	0.0
O	H(1)		−0.430	−0.571	−0.829	0.0	0.0
O	H(2)		−0.430	−0.571	0.829	0.0	0.0
H(1)	H(1)		12.429	6.549	9.515	9.515	13.824
H(1)	H(2)		2.620	2.316	−3.365	3.365	−4.889
O			0.959	0.617	0.0	0.0	0.0
H(1)			14.620	8.294	6.150	12.050	8.935
H(2)			14.620	8.294	−6.150	−12.050	8.935
Total		(K,K)	30.198	17.204	0.0	0.0	17.871

TABLE XV. Partition of the electric polarizability at $\omega=0$, in a.u.

Atomic Contributions I	J	Formalism	α_{xx}	α_{yy}	α_{yz}	α_{zy}	α_{zz}
O			5.587	5.567	0.0	0.0	4.988
H(1)			0.990	1.772	−1.051	−0.943	1.660
H(2)			0.990	1.772	1.051	0.943	1.660
Total		(F,R)	7.567	9.111	0.0	0.0	8.309
O			5.573	5.574	0.0	0.0	5.006
H(1)			0.990	1.773	−1.049	−0.941	1.662
H(2)			0.990	1.773	1.049	0.941	1.662
Total		(F,P)	7.554	9.120	0.0	0.0	8.330
O	O		5.245	5.334	0.0	0.0	4.207
O	H(1)		0.169	0.130	−0.144	0.147	0.382
O	H(2)		0.169	0.130	0.144	−0.147	0.382
H(1)	H(1)		0.594	1.501	−0.960	−0.960	1.122
H(1)	H(2)		0.115	0.099	−0.161	0.161	0.091
O			5.582	5.593	0.0	0.0	4.972
H(1)			0.878	1.730	−0.974	−0.944	1.596
H(2)			0.878	1.730	0.974	0.944	1.596
Total		(F,F)	7.337	9.053	0.0	0.0	8.163

TABLE XVI. Partition of the electric polarizability at $\omega=0.3$, in a.u.

Atomic Contributions I	J	Formalism	α_{xx}	α_{yy}	α_{yz}	α_{zy}	α_{zz}
Total		(R,R)	21.246	11.776	0.0	0.0	12.042
Total		(P,R)	21.414	11.788	0.0	0.0	12.074
Total		(P,P)	21.591	11.801	0.0	0.0	12.108
O			7.823	6.709	0.0	0.0	6.074
H(1)			5.575	2.490	−2.182	−1.449	2.818
H(2)			5.575	2.490	2.182	1.449	2.818
Total		(F,R)	18.974	11.690	0.0	0.0	11.709
O			7.843	6.719	0.0	0.0	6.101
H(1)			5.637	2.492	−2.180	−1.447	2.821
H(2)			5.637	2.492	2.180	1.447	2.821
Total		(F,P)	19.118	11.702	0.0	0.0	11.743
O	O		6.826	6.520	0.0	0.0	5.088
O	H(1)		0.445	0.115	−0.204	0.145	0.481
O	H(2)		0.445	0.115	0.204	−0.145	0.481
H(1)	H(1)		2.530	2.455	−1.707	−1.707	1.852
H(1)	H(2)		1.716	−0.136	−0.459	0.459	0.344
O			7.715	6.749	0.0	0.0	6.050
H(1)			4.691	2.433	−2.021	−1.452	2.678
H(2)			4.691	2.433	2.021	1.452	2.678
Total		(F,F)	17.097	11.616	0.0	0.0	11.406

TABLE XVII. Dipole nuclear electric shielding in (F,F) formalism at $\omega=0$.

Atomic Contributions I	J	γ^I_{xx}	γ^I_{yy}	γ^I_{zy}	γ^I_{yz}	γ^I_{zz}
O	O	0.994	1.034	0	0	0.967
O	H(1)	0.039	0.012	0.030	0.016	0.035
O	H(2)	0.039	0.012	−0.030	−0.016	0.035
O		1.072	1.058	0	0	1.037
H(1)	O	0.310	0.094	0.129	0.243	0.280
H(1)	H(1)	0.279	0.562	−0.240	−0.240	0.460
H(1)	H(2)	0.025	0.042	0.053	−0.053	0.017
H(1)		0.614	0.698	−0.059	−0.050	0.757

TABLE XVIII. Dipole nuclear electric shielding in (F,F) formalism at $\omega=0.3$ a.u.

Atomic Contributions I	J	γ^I_{xx}	γ^I_{yy}	γ^I_{zy}	γ^I_{yz}	γ^I_{zz}
O	O	1.071	1.108	0	0	1.024
O	H(1)	0.044	0.013	0.032	0.014	0.040
O	H(2)	0.044	0.013	−0.032	−0.014	0.040
O		1.158	1.134	0	0	1.105
H(1)	O	0.350	0.104	0.110	0.256	0.323
H(1)	H(1)	0.507	0.783	−0.394	−0.394	0.627
H(1)	H(2)	0.179	0.030	0.095	−0.095	0.048
H(1)		1.036	0.918	−0.189	−0.232	0.998

optical activity and shielding tensors reported here. A similar judgement is achieved by inspection of the atomic contributions to paramagnetic susceptibility (Tables XIII and XIV), to polarizability (Tables XV and XVI), and to electric shielding (Tables XVII and XVIII). Sum rules (36), (49), and (81) are fairly well satisfied, which is another way of showing the excellent overall characteristics of our wave function.

Using the atomic polarizability in Table XIII, we have computed the average static polarizability of hydrogen peroxide, $\alpha(0)=13.7$ a.u., to be compared with the experimental value 15.43.[27] As the electron correlation contributions are about 10% of the whole quantity,[21] we can reasonably argue that our estimate for hydrogen peroxide is close to the limit value obtainable via an uncorrelated RPA calculation. Since the theoretical polarizability of water evaluated here is comparable in accuracy with the best ones available so far, and virtually coincident with the RPA limit,[10] our results may imply transferability of the atomic polarizabilities in Table XIII.

VI. CONCLUSIONS

We have introduced a series of new molecular tensors which could be used to rationalize the behavior of a molecule perturbed by periodic electromagnetic fields in terms of effective average fields induced at the nuclei. These tensors possess important properties: they satisfy translational and rotational sum rules, which are proven to be very general quantum-mechanical relations, namely TRK sum rules, gauge-invariance conditions, commutation relations, hypervirial theorems, and constraints expressing the conservation of the current density field. All of these are different but deeply interrelated aspects of one and the same physical background. The shielding tensors are related to each other, and are connected with the electric polarizability, the optical activity, and the paramagnetic susceptibility via simple equations. The present findings allow one to write down a partition of molecular tensors in terms of atomic contributions, according to an additivity scheme.

One could reasonably infer that the present results show some fundamental relations among second-order properties in terms of a general and unitary perspective. A numerical test on the water molecule, based on a high-quality RPA calculation, gives accurate sum rules and a first series of theoretical predictions for the new quantities.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge important suggestions and useful comments raised by Professor S. T. Epstein. We also thank Professor A. D. Buckingham, Dr. P. W. Fowler, and Dr. P. A. Galwas for kindly making available a manuscript prior to submission. Computer time generously provided by the Centro di Calcolo dell'Università degli Studi di Modena and financial support from the Ministero della Pubblica Istruzione (Italy) are gratefully acknowledged.

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