Quantum-mechanical sum rules and gauge invariance: A study of the HF molecule

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The perturbed Hamiltonian for magnetic dipole transitions is rewritten in terms of the torque operator, instead of the angular momentum operator, which, owing to its nondifferential form, permits tactical advantages in actual calculations of magnetic susceptibility. The translational gauge invariance of the magnetic properties is used to obtain a large series of sum rules involving linear and angular momenta and torque, force, and position operators. These are found to be very general quantum-mechanical relations, restating in a synthetic and unitary form the Thomas-Reiche-Kuhn sum rule, the basic operator commutation properties, the hypervirial theorem, and the conservation of the current-density vector, which are reduced to the same theoretical framework. Accurate calculations of the magnetic properties of the HF molecule, based on the equation-of-motion approach, reveal that the gauge-invariant sum rules can be used for rigorous tests of the quality of approximate molecular wave functions.

I. INTRODUCTION

The quality of approximate electronic wave functions for atoms and molecules can be assessed *a priori*, by examining the degree up to which certain sum rules are fulfilled.[1] These sum rules are usually derived as very general quantum-mechanical relations, holding for exact wave functions. It has been recently established, however, that also approximate methods, namely the random-phase approximation[2] (RPA), which is the same as the time-dependent Hartree-Fock[3] (TDHF), or coupled Hartree-Fock[4,5(a)] (CHF) scheme, satisfy the Thomas-Reiche-Kuhn (TRK) sum rule[1] and the Arrighini-Maestro-Moccia (AMM) gauge-invariant constraints[6] *exactly*, provided that complete sets of expansion are retained in actual calculations.[7,8]

Accordingly, it has been found that the quantum-mechanical constraints[1,6] are virtually obeyed (up to 99%) in extended calculations,[9] allowing for large basis sets of contracted Gaussian-type orbitals (CGTO). Precise CHF and RPA estimates[9] of the TRK and AMM sum rules are usually accompanied by accurate theoretical determination of second-order properties (magnetizability and nuclear magnetic shielding in particular[9(a),9(b)]) which are in close agreement with corresponding experimental data. Therefore, it can be reasonably stated that the proper use of a large set of sum rules can give essential indications, in order to establish the reliability of approximate calculations of second-order properties, especially when experimental data are not available for comparison.

The present paper sets out to obtain a series of translational gauge-invariant constraints for the magnetizability and the nuclear magnetic shielding. A new form of the perturbed Hamiltonian for the magnetic dipole radiation is given in Sec. II, introducing the torque operator. The relative torque formalism is used in Sec. III to obtain the equations for the magnetic susceptibility and the nuclear magnetic shielding. Gauge transformations are examined in Sec. IV. Conditions for gauge invariance and their physical meaning are discussed in Sec. V. Section VI is dedicated to a computational test for the hydrogen fluoride molecule.

II. THE TORQUE FORMALISM FOR MAGNETIC DIPOLE TRANSITIONS

The Hamiltonian for one particle of mass m and charge q is[10]

$$\mathscr{H}=\frac{1}{2m}\left[\mathbf{p}-\frac{q}{c}\mathbf{A}\right]^2+V+q\phi\ . \tag{1}$$

Within the Coulomb gauge

$$\nabla\cdot\mathbf{A}=0=\phi\ . \tag{2}$$

The vector potential is expanded in MacLaurin series

$$\mathbf{A}(\mathbf{r},t)=\mathbf{A}(0,t)+[(\mathbf{r}\cdot\nabla)\mathbf{A}]_0+\cdots\ , \tag{3}$$

where ∇ operates only on $\mathbf{A}$ and the result is to be evaluated at the origin. From a straightforward manipulation we work out the first-order Hamiltonian

$$\mathscr{H}^{B_0}=-(q/2mc)\mathbf{B}_0\cdot\boldsymbol{l}\ , \tag{4}$$

$$\mathbf{B}_0=(\nabla\times\mathbf{A})_0\ , \tag{5}$$

$$\boldsymbol{l}=\mathbf{r}\times\mathbf{p}\ . \tag{6}$$

The form (4) is usually assumed in the general treatment of magnetic dipole transitions.[11] However, in practical applications, some difficulties can be found in handling Hamiltonian (4), because of the differential form of the angular momentum operator $\boldsymbol{l}$.

We derive hereafter an alternative Hamiltonian containing the torque operator, which is merely multiplicative in the coordinate representation. Its matrix elements are easy to evaluate when Slater-type orbitals (STO's) or CGTO's are retained.

The total Hamiltonian is defined, through first order in a function G, to within a total time derivative, provided that r, p, and $\mathscr{H}_0$ are not changed. Within quantum mechanics this follows by making the unitary transformation

$$\mathscr{H}\rightarrow\mathscr{H}'=\exp[(i/\hbar)G]\mathscr{H}\exp[-(i/\hbar)G]-\frac{\partial}{\partial t}G$$

and expanding through first order in G. Classically we can argue that one is always free to change the Lagrangian $L\rightarrow L+dG/dt$, and through first order in G this implies $\mathscr{H}'=\mathscr{H}-dG/dt$, where

$$\frac{dG}{dt}=\frac{i}{\hbar}[\mathscr{H}_0,G]+\frac{\partial G}{\partial t}\ , \tag{7}$$

where, in our case,

$$\mathscr{H}_0=\frac{1}{2m}p^2+V\ . \tag{8}$$

The form of G is properly chosen, so that

$$\frac{\partial G}{\partial t}=\mathscr{H}^{B_0}\ . \tag{9}$$

Introducing the Hertz vector[12] $\mathbf{Z}=\mathbf{Z}(\mathbf{r},t)$, so defined that

$$\mathbf{A}=-(1/c)\frac{\partial}{\partial t}\mathbf{Z},\quad \phi=\nabla\cdot\mathbf{Z}\ , \tag{10}$$

$$\mathbf{B}=-(1/c)\frac{\partial}{\partial t}(\nabla\times\mathbf{Z})\ , \tag{11}$$

and choosing, in the Coulomb gauge (2),

$$G=\frac{q}{2mc^2}(\nabla\times\mathbf{Z})_0\cdot\boldsymbol{l}\ , \tag{12}$$

we obtain the new Hamiltonian

$$\mathscr{H}^{(\nabla\times\mathbf{Z})_0}=-\frac{q}{2mc^2}(\nabla\times\mathbf{Z})_0\cdot\mathbf{k}\ , \tag{13}$$

where $\mathbf{k}$ is the torque on the particle with respect to the origin of coordinates

$$\mathbf{k}=\frac{d\boldsymbol{l}}{dt}=\frac{i}{\hbar}[\mathscr{H}_0,\boldsymbol{l}]\ , \tag{14}$$

These equations are immediately generalized to the case of a closed-shell molecule with n electrons and N nuclei, with coordinates $\mathbf{r}_i$ and $\mathbf{R}_I$ and charges $-e$ and Z_Ie, respectively, in the form

$$\mathscr{H}^{(\nabla\times\mathbf{Z})_0}=(\nabla\times\mathbf{Z})_0\cdot\mathbf{h}^{(\nabla\times\mathbf{Z})_0}\ , \tag{15a}$$

$$\mathbf{h}^{(\nabla\times\mathbf{Z})_0}=\frac{e}{2mc^2}\mathbf{K}_n^N\ , \tag{15b}$$

where

$$\mathbf{K}_n^N(\mathbf{r}_0)=e^2\sum_{I=1}^{N}\sum_{i=1}^{n}Z_I\,|\,\mathbf{r}_i-\mathbf{R}_I\,|^{-3}(\mathbf{r}_i-\mathbf{R}_I)\times(\mathbf{R}_I-\mathbf{r}_0)\ . \tag{16}$$

is the torque about the origin $\mathbf{r}_0$, exerted by the nuclei on the electrons, in the absence of magnetic perturbations.

We point out that the procedure we adopted to obtain (15) amounts to performing an infinitesimal canonical transformation of the Hamiltonian.[13,10] Owing to (14) the matrix elements of (15) are related to those of the total electronic angular momentum about $\mathbf{r}_0$,

$$\mathbf{L}(\mathbf{r}_0)=\sum_{i=1}^{n}\boldsymbol{l}_i(\mathbf{r}_0),\quad \boldsymbol{l}_i(\mathbf{r}_0)=(\mathbf{r}_i-\mathbf{r}_0)\times\mathbf{p}_i \tag{17}$$

by the equation

$$\langle a\,|\,\mathbf{K}_n^N\,|\,b\,\rangle=\frac{i}{\hbar}(E_a-E_b)\langle a\,|\,\mathbf{L}\,|\,b\,\rangle\ , \tag{18}$$

where E_a,E_b are the energies of the stationary states Ψ_a,Ψ_b.

III. MAGNETIC PROPERTIES WITHIN THE TORQUE FORMALISM

In the presence of a spatially uniform, static magnetic field $\mathbf{B}$ and an intrinsic magnetic dipole moment $\boldsymbol{\mu}_I$ on nucleus I, the operators entering the total electronic Born-Oppenheimer Hamiltonian are

$$\mathscr{H}^{\mathbf{B}}=\mathbf{B}\cdot\mathbf{h}^{\mathbf{B}}\ , \tag{19}$$

$$\mathscr{H}^{\mathbf{BB}}=\mathbf{B}\cdot\mathbf{h}^{\mathbf{BB}}\cdot\mathbf{B}\ , \tag{20}$$

$$\mathscr{H}^{\mu_I}=\boldsymbol{\mu}_I\cdot\mathbf{h}^{\mu_I}\ , \tag{21}$$

$$\mathscr{H}^{\mu_I\mathbf{B}}=\boldsymbol{\mu}_I\cdot\mathbf{h}^{\mu_I\mathbf{B}}\cdot\mathbf{B}\ , \tag{22}$$

where the reduced operators on the right-hand side are defined as

$$\mathbf{h}^{\mathbf{B}}(\mathbf{r}_0)=(e/2mc)\mathbf{L}(\mathbf{r}_0)\ , \tag{23}$$

$$\mathbf{h}^{\mathbf{BB}}(\mathbf{r}_0)=(1/8mc^2)\sum_{i=1}^{n}\{[\mathbf{m}_i(\mathbf{r}_0)]^2\mathbb{1}-\mathbf{m}_i(\mathbf{r}_0)\mathbf{m}_i(\mathbf{r}_0)\}\ , \tag{24}$$

$$\mathbf{h}^{\mu_I}\equiv-\mathbf{B}_I^n=(e/mc)\mathbf{M}_I\ ,\qquad \mathbf{M}_I=\sum_{i=1}^{n}|\,\mathbf{r}_i-\mathbf{R}_I\,|^{-3}\boldsymbol{l}_i(\mathbf{R}_I)\ , \tag{25}$$

$$\mathbf{h}^{\mu_I\mathbf{B}}(\mathbf{r}_0)=-(1/2mc^2)\sum_{i=1}^{n}[\mathbf{m}_i(\mathbf{r}_0)\cdot\mathbf{E}_I^i\mathbb{1}-\mathbf{m}_i(\mathbf{r}_0)\mathbf{E}_I^i]\ . \tag{26}$$

The electric field on nucleus I, due to electron i, is in operator form

$$\mathbf{E}_I^i=e\,|\,\mathbf{r}_i-\mathbf{R}_I\,|^{-3}(\mathbf{r}_i-\mathbf{R}_I) \tag{27}$$

and

$$\mathbf{m}_i(\mathbf{r}_0)=-e(\mathbf{r}_i-\mathbf{r}_0) \tag{28}$$

is the dipole moment operator for electron i with respect to the origin. The diamagnetic susceptibility is defined

$$\chi^d(\mathbf{r}_0) = -2\langle 0 | \mathbf{h}^{\mathbf{BB}}(\mathbf{r}_0) | 0 \rangle = -\frac{e^2}{4mc^2}\left\langle 0 \left| \sum_{i=1}^{n} [(\mathbf{r}_i - \mathbf{r}_0)^2 \mathbb{1} - (\mathbf{r}_i - \mathbf{r}_0)(\mathbf{r}_i - \mathbf{r}_0)] \right| 0 \right\rangle \tag{29}$$

and the paramagnetic susceptibility within the angular momentum L,L formalism is

$$\chi^p(\mathbf{r}_0) = -2 \sum_j{}' \langle 0 | \mathbf{h}^B(\mathbf{r}_0) | j \rangle \langle j | \mathbf{h}^B(\mathbf{r}_0) | 0 \rangle (E_0 - E_j)^{-1} = \frac{e^2}{4m^2c^2} (\mathbf{L},\mathbf{L})_{-1} , \tag{30}$$

$$(\mathbf{L},\mathbf{L})_{-1} = 2 \sum_j{}' \langle 0 | \mathbf{L}(\mathbf{r}_0) | j \rangle \langle j | \mathbf{L}(\mathbf{r}_0) | 0 \rangle (E_j - E_0)^{-1} . \tag{31}$$

The diamagnetic shielding tensor of nucleus I is

$$\sigma^{dI}(\mathbf{r}_0) = \langle 0 | \mathbf{h}^{\mu_I \mathbf{B}}(\mathbf{r}_0) | 0 \rangle = \frac{e^2}{2mc^2} \left\langle 0 \left| \sum_{i=1}^{n} \left[(\mathbf{r}_i - \mathbf{r}_0) \cdot \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \mathbb{1} - (\mathbf{r}_i - \mathbf{r}_0) \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \right] \right| 0 \right\rangle \tag{32}$$

and the paramagnetic shielding tensor in the L formalism is

$$\sigma^{pI}(\mathbf{r}_0) = 2 \sum_j{}' \langle 0 | \mathbf{h}^{\mu_I} | j \rangle \langle j | \mathbf{h}^{\mathbf{B}} | 0 \rangle (E_0 - E_j)^{-1}$$
$$= -\frac{e^2}{2m^2c^2} (\mathbf{M}_I, \mathbf{L})_{-1} , \tag{33}$$

$$(\mathbf{M}_I, \mathbf{L})_{-1} = 2 \sum_j{}' \langle 0 | \mathbf{M}_I | j \rangle \langle j | \mathbf{L}(\mathbf{r}_0) | 0 \rangle (E_j - E_0)^{-1} . \tag{34}$$

A set of real orthonormal states $|j\rangle$ is assumed throughout this paper and the convention for the σ tensor indices is such that the interaction energy is written

$$W(\mu_I, \mathbf{B}) = \mu_I \cdot \sigma^I \cdot \mathbf{B} . \tag{35}$$

Allowing for Eq. (18) the paramagnetic susceptibility can be given alternative forms.

(i) The mixed torque—angular-momentum K,L formalism is

$$\chi^p(\mathbf{r}_0) = (e^2/4m^2c^2)(\mathbf{K},\mathbf{L})_{-2} = (e^2/4m^2c^2)(\mathbf{L},\mathbf{K})_{-2} , \tag{36}$$

$$(\mathbf{K},\mathbf{L})_{-2} = 2i\hbar \sum_j{}' (E_j - E_0)^{-2} \langle 0 | \mathbf{K}_n^N(\mathbf{r}_0) | j \rangle \times \langle j | \mathbf{L}(\mathbf{r}_0) | 0 \rangle , \tag{37a}$$

$$(\mathbf{L},\mathbf{K})_{-2} = -2i\hbar \sum_j{}' (E_j - E_0)^{-2} \langle 0 | \mathbf{L}(\mathbf{r}_0) | j \rangle \times \langle j | \mathbf{K}_n^N(\mathbf{r}_0) | 0 \rangle . \tag{37b}$$

(ii) The full torque K,K formalism is

$$\chi^p(\mathbf{r}_0) = (e^2/4m^2c^2)(\mathbf{K},\mathbf{K})_{-3} , \tag{38}$$

$$(\mathbf{K},\mathbf{K})_{-3} = 2\hbar^2 \sum_j{}' (E_j - E_0)^{-3} \langle 0 | \mathbf{K}_n^N(\mathbf{r}_0) | j \rangle \times \langle j | \mathbf{K}_n^N(\mathbf{r}_0) | 0 \rangle . \tag{39}$$

The K paramagnetic shielding is

$$\sigma^{pI}(\mathbf{r}_0) = -(e^2/2m^2c^2)(\mathbf{M}_I, \mathbf{K})_{-2} , \tag{40}$$

$$(\mathbf{M}_I, \mathbf{K})_{-2} = -2i\hbar \sum_j{}' \langle 0 | \mathbf{M}_I | j \rangle \langle j | \mathbf{K}_n^N(\mathbf{r}_0) | 0 \rangle \times (E_j - E_0)^{-2} . \tag{41}$$

IV. GAUGE TRANSFORMATIONS

The vector potential in Eq. (1) is defined to within the gradient of an arbitrary scalar function[14] $\nabla f(\mathbf{r})$. Consider a change of origin

$$\mathbf{r}_0 \equiv \mathbf{r}' \to \mathbf{r}'', \quad \mathbf{r}'' - \mathbf{r}' = \mathbf{d} . \tag{42}$$

If the vector potential on the ith electron undergoes the gauge transformation

$$\mathbf{A}_i' \to \mathbf{A}_i'' \equiv \mathbf{A}(\mathbf{r}_i - \mathbf{r}''), \quad f(\mathbf{r}_i) = (\mathbf{d} \cdot \mathbf{A}_i') , \tag{43}$$

$$\mathbf{A}_i'' = \mathbf{A}_i' + \nabla_i (\mathbf{d} \cdot \mathbf{A}_i') , \tag{44}$$

the molecular reduced Hamiltonians defined via Eqs. (15b), (22), (23), and (25) transform

$$\mathbf{h}^{\mathbf{B}}(\mathbf{r}'') = \mathbf{h}^{\mathbf{B}}(\mathbf{r}') + \mathbf{h}^{\mathbf{d} \times \mathbf{B}}, \quad \mathbf{h}^{\mathbf{d} \times \mathbf{B}} = -(e/2mc)\mathbf{d} \times \mathbf{P} , \tag{45}$$

$$\mathbf{h}^{\mathbf{BB}}(\mathbf{r}'') = \mathbf{h}^{\mathbf{BB}}(\mathbf{r}') - \frac{e^2}{8mc^2} [2\mathbf{d} \cdot \mathbf{R}(\mathbf{r}') \mathbb{1} - \mathbf{d}\mathbf{R}(\mathbf{r}') - \mathbf{R}(\mathbf{r}')\mathbf{d}] + \frac{e^2}{8mc^2} n (d^2 \mathbb{1} - \mathbf{d}\mathbf{d}) , \tag{46}$$

$$\mathbf{h}^{\mu_I \mathbf{B}}(\mathbf{r}'') = \mathbf{h}^{\mu_I \mathbf{B}}(\mathbf{r}') - \frac{e}{2mc^2} (\mathbf{d} \cdot \mathbf{E}_I^n \mathbb{1} - \mathbf{d}\mathbf{E}_I^n) , \tag{47}$$

$$\mathbf{h}^{\nabla \times \mathbf{Z}}(\mathbf{r}'') = \mathbf{h}^{\nabla \times \mathbf{Z}}(\mathbf{r}') + (e/2mc^2) \mathbf{F}_n^N \times \mathbf{d} , \tag{48}$$

where the electronic contribution to the dipole moment is

$$-e\mathbf{R}(\mathbf{r}_0) = \sum_{i=1}^{n} \mathbf{m}_i(\mathbf{r}_0) = -e \sum_{i=1}^{n} (\mathbf{r}_i - \mathbf{r}_0) . \tag{49}$$

The total canonical momentum of electrons is

$$m \frac{d\mathbf{R}}{dt} = \mathbf{P} = \sum_{i=1}^{n} \mathbf{p}_i . \tag{50}$$

The operator for the electric field exerted by the electrons on nucleus I is [see Eq. (27)]

$$\mathbf{E}_I^n = \sum_{i=1}^{n} \mathbf{E}_I^i \tag{51}$$

and the operator expressing the force of the nuclei on the electrons is

$$\frac{d\mathbf{P}}{dt} = \mathbf{F}_n^N = -e^2 \sum_{I=1}^{N} \sum_{i=1}^{n} Z_I \,|\, \mathbf{r}_i - \mathbf{R}_I \,|^{-3} (\mathbf{r}_i - \mathbf{R}_I) \; . \tag{52}$$

Owing to (45) and (47), in a translation of gauge origin, the magnetic susceptibilities (29), (30), (36), and (38) transform to

$$\chi^d_{\alpha\alpha}(\mathbf{r}'') = \chi^d_{\alpha\alpha}(\mathbf{r}') + \frac{e^2}{4mc^2}(2\langle R_\beta \rangle d_\beta + 2\langle R_\gamma \rangle d_\gamma - n d_\beta^2 - n d_\gamma^2) \; , \tag{53}$$

$$\chi^p_{\alpha\alpha}(\mathbf{r}'') = \chi^p_{\alpha\alpha}(\mathbf{r}') - \frac{e^2}{4m^2c^2}[2(P_\gamma, L_\alpha)_{-1} d_\beta - 2(L_\alpha, P_\beta)_{-1} d_\gamma - (P_\gamma, P_\gamma)_{-1} d_\beta^2 - (P_\beta, P_\beta)_{-1} d_\gamma^2] \;\; \text{for } L,L \; , \tag{54}$$

$$\chi^p_{\alpha\alpha}(\mathbf{r}'') = \chi^p_{\alpha\alpha}(\mathbf{r}') - \frac{e^2}{4m^2c^2}\{ [(P_\gamma, K_\alpha)_{-2} + (F_\gamma, L_\alpha)_{-2}] d_\beta - [(L_\alpha, F_\beta)_{-2} + (K_\alpha, P_\beta)_{-2}] d_\gamma - (F_\beta, P_\beta)_{-2} d_\gamma^2 - (F_\gamma, P_\gamma)_{-2} d_\beta^2 \} \;\; \text{for } K,L \tag{55}$$

$$\chi^p_{\alpha\alpha}(\mathbf{r}'') = \chi^p_{\alpha\alpha}(\mathbf{r}') - \frac{e^2}{4m^2c^2}[2(F_\gamma, K_\alpha)_{-3} d_\beta - 2(K_\alpha, F_\beta)_{-3} d_\gamma - (F_\gamma, F_\gamma)_{-3} d_\beta^2 - (F_\beta, F_\beta)_{-3} d_\gamma^2] \;\; \text{for } K,K \tag{56}$$

$$\chi^d_{\alpha\beta}(\mathbf{r}'') = \chi^d_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{4mc^2}(\langle R_\alpha \rangle d_\beta + \langle R_\beta \rangle d_\alpha - n d_\alpha d_\beta) \; , \tag{57}$$

$$\chi^p_{\alpha\beta}(\mathbf{r}'') = \chi^p_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{4m^2c^2}[(L_\alpha, P_\gamma)_{-1} d_\alpha - (P_\gamma, L_\beta)_{-1} d_\beta - (P_\gamma, P_\gamma)_{-1} d_\alpha d_\beta] \;\; \text{for } L,L \tag{58}$$

$$\chi^p_{\alpha\beta}(\mathbf{r}'') = \chi^p_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{4m^2c^2}[(K_\alpha, P_\gamma)_{-2} d_\alpha - (F_\gamma, L_\beta)_{-2} d_\beta - (F_\gamma, P_\gamma)_{-2} d_\alpha d_\beta] \;\; \text{for } K,L \tag{59}$$

$$\chi^p_{\alpha\beta}(\mathbf{r}'') = \chi^p_{\alpha\beta}(\mathbf{r}') + \frac{e^2}{4m^2c^2}[(K_\alpha, F_\gamma)_{-3} d_\alpha - (F_\gamma, K_\beta)_{-3} d_\beta - (F_\gamma, F_\gamma)_{-3} d_\alpha d_\beta] \;\; \text{for } K,K \; . \tag{60}$$

The nuclear magnetic shielding transforms to

$$\sigma^{dI}_{\alpha\alpha}(\mathbf{r}'') = \sigma^{dI}_{\alpha\alpha}(\mathbf{r}') - \frac{e}{2mc^2}(\langle E^n_{I\beta} \rangle d_\beta + \langle E^n_{I\gamma} \rangle d_\gamma) \; , \tag{61}$$

$$\sigma^{pI}_{\alpha\alpha}(\mathbf{r}'') = \sigma^{pI}_{\alpha\alpha}(\mathbf{r}') + \frac{e^2}{2m^2c^2}[(M_{I\alpha}, P_\gamma)_{-1} d_\beta - (M_{I\alpha}, P_\beta)_{-1} d_\gamma] \;\; \text{for } L \; , \tag{62}$$

$$\sigma^{pI}_{\alpha\alpha}(\mathbf{r}'') = \sigma^{pI}_{\alpha\alpha}(\mathbf{r}') + \frac{e^2}{2m^2c^2}[(M_{I\alpha}, F_\gamma)_{-2} d_\beta - (M_{I\alpha}, F_\beta)_{-2} d_\gamma] \;\; \text{for } K \; , \tag{63}$$

$$\sigma^{dI}_{\alpha\beta}(\mathbf{r}'') = \sigma^{dI}_{\alpha\beta}(\mathbf{r}') + \frac{e}{2mc^2}\langle E^n_{I\beta} \rangle d_\alpha \; , \tag{64}$$

$$\sigma^{pI}_{\alpha\beta}(\mathbf{r}'') = \sigma^{pI}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{2m^2c^2}(M_{I\alpha}, P_\gamma)_{-1} d_\alpha \;\; \text{for } L \; , \tag{65}$$

$$\sigma^{pI}_{\alpha\beta}(\mathbf{r}'') = \sigma^{pI}_{\alpha\beta}(\mathbf{r}') - \frac{e^2}{2m^2c^2}(M_{I\alpha}, F_\gamma)_{-2} d_\alpha \;\; \text{for } K \; . \tag{66}$$

In (53) the quantities $(\underline{P},\underline{L}) = (\underline{L},\underline{P})$ and $(\underline{P},\underline{P})$ are defined analogously to (31), the quantities $(\underline{K},\underline{P}) = (\underline{P},\underline{K})$, $(\underline{F},\underline{P}) = (\underline{P},\underline{F})$, and $(\underline{F},\underline{L}) = (\underline{L},\underline{F})$ are defined analogously to (37), and $(\underline{F},\underline{F})$ is defined analogously to (39). The tensor $(\underline{M}_I,\underline{P})$ is defined analogously to (34).

Exploiting the definition of time derivative for a vector operator $\mathbf{T}$, which does not contain the time explicitly,

$$\frac{d}{dt}\mathbf{T} = \dot{\mathbf{T}} = \frac{i}{\hbar}[\mathscr{H}_0, \mathbf{T}] \tag{67}$$

we can also introduce the tensors

$$(\mathbf{P},\mathbf{R})_0 = (2im/\hbar) \sum_j{}' \langle 0 \,|\, \mathbf{P} \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, 0 \rangle \; , \tag{68}$$

$$(\mathbf{R},\mathbf{P})_0 = -(2im/\hbar) \sum_j{}' \langle 0 \,|\, \mathbf{R} \,|\, j \rangle \langle j \,|\, \mathbf{P} \,|\, 0 \rangle \; , \tag{69}$$

and the tensors $(\underline{L},\underline{R})_0 = (\underline{R},\underline{L})_0$ and $(\underline{M}_I,\underline{R})_0 = (\underline{R},\underline{M}_I)_0$ are similarly defined. Other tensors are similarly defined, for instance,

$$(\mathbf{R},\mathbf{R})_1 = (2m/\hbar^2) \sum_j{}' \langle 0 \,|\, \mathbf{R} \,|\, j \rangle \langle j \,|\, \mathbf{R} \,|\, 0 \rangle (E_j - E_0) \; .$$

V. SUM RULES FOR GAUGE INVARIANCE

Owing to gauge invariance

$$\chi(\mathbf{r}'')=\chi^d(\mathbf{r}'')+\chi^p(\mathbf{r}'')=\chi(\mathbf{r}')=\chi^d(\mathbf{r}')+\chi^p(\mathbf{r}') . \qquad (70)$$

From Eqs. (53)—(60) and (67)—(69) we obtain sum rules for the translational invariance of the magnetizability:

$$\begin{aligned} m\langle R_\beta\rangle(1-\delta_{\alpha\gamma}) &= (P_\gamma,L_\alpha)_{-1}=-(P_\alpha,L_\gamma)_{-1} \\ &= -(K_\gamma,P_\alpha)_{-2}=(K_\alpha,P_\gamma)_{-2} \\ &= -(K_\gamma,F_\alpha)_{-3}=(K_\alpha,F_\gamma)_{-3} \\ &= (F_\gamma,L_\alpha)_{-2}=-(F_\alpha,L_\gamma)_{-2} \\ &= (R_\gamma,L_\alpha)_0=-(L_\gamma,R_\alpha)_0 \\ &= -(K_\gamma,R_\alpha)_{-1}=(K_\alpha,R_\gamma)_{-1} , \end{aligned} \qquad (71)$$

$$\begin{aligned} mn\delta_{\alpha\beta} &= (P_\alpha,P_\beta)_{-1}=(P_\alpha,F_\beta)_{-2}=(F_\alpha,F_\beta)_{-3} \\ &= (R_\alpha,P_\beta)_0=(R_\alpha,F_\beta)_{-1}=(R_\alpha,R_\beta)_{+1} . \end{aligned} \qquad (72)$$

From Eqs. (61)—(67) and an equation analogous to (70) we obtain the sum rules for the translational invariance of the magnetic shielding:

$$\begin{aligned} \frac{m}{e}\langle E^n_{I\beta}\rangle(1-\delta_{\alpha\gamma}) &= (M_{I\alpha},P_\gamma)_{-1}=-(M_{I\gamma},P_\alpha)_{-1} \\ &= (M_{I\alpha},F_\gamma)_{-2}=-(M_{I\gamma},F_\alpha)_{-2} \\ &= (M_{I\alpha},R_\gamma)_0=-(M_{I\gamma},R_\alpha)_0 . \end{aligned} \qquad (73)$$

It is immediately recognized that the gauge-invariant constraints (72) are the TRK sum rule written in length, velocity, acceleration, and mixed formalisms.[9(d)] In addition, by straightforward manipulation,

$$(P_\alpha,R_\beta)_0+(R_\beta,P_\alpha)_0=\frac{2im}{\hbar}\langle 0\,|\,[P_\alpha,R_\beta]\,|\,0\rangle=2mn\delta_{\alpha\beta} , \qquad (72')$$

i.e., the same equations are a restatement of the basic commutation rule between $\mathbf{P}$ and $\mathbf{R}$. Analogously

$$\begin{aligned} (L_\alpha,P_\gamma)_{-1}+(P_\gamma,L_\alpha)_{-1} &= (2im/\hbar)\langle 0\,|\,[L_\alpha,R_\gamma]\,|\,0\rangle \\ &= 2m\langle 0\,|\,R_\beta\,|\,0\rangle(1-\delta_{\alpha\gamma}) , \end{aligned} \qquad (71')$$

$$\begin{aligned} (M_{I\alpha},P_\gamma)_{-1}+(P_\gamma,M_{I\alpha})_{-1} &= (2im/\hbar)\langle 0\,|\,[M_{I\alpha},R_\gamma]\,|\,0\rangle \\ &= \frac{2m}{e}\langle 0\,|\,E^n_{I\beta}\,|\,0\rangle(1-\delta_{\alpha\gamma}) . \end{aligned} \qquad (23')$$

Equations (71)—(73) are very general quantum-mechanical relationships, synthesize various aspects, and possess a deep physical meaning. In the following we prove that they embody the conservation theorem for the current density.[15,16] To this end consider the gauge translation [(42) and (43)] as inducing an infinitesimal canonical transformation. The generating function is

$$g=-\frac{e}{c}\sum_k \mathbf{d}\cdot\mathbf{A}'_k=-\frac{e}{2c}\mathbf{d}\times\mathbf{B}\cdot\mathbf{R}(\mathbf{r}') \qquad (74)$$

so that, to first order in $\mathbf{B}$,

$$\Psi\to\Psi\exp\left[\frac{i}{\hbar}g\right]=\Psi_0+\mathbf{B}\cdot\Psi^B-\frac{ie}{2\hbar c}\mathbf{d}\times\mathbf{B}\cdot\mathbf{R}(\mathbf{r}')\Psi_0+\cdots , \qquad (75)$$

$$\mathscr{H}\to\exp\left[\frac{i}{\hbar}g\right]\mathscr{H}\exp\left[-\frac{i}{\hbar}g\right]=\mathscr{H}+\frac{e}{2mc}\mathbf{d}\times\mathbf{B}\cdot\mathbf{P}+\cdots . \qquad (76)$$

One can compare (75) with the perturbation expansion

$$\Psi=\Psi_0+\mathbf{B}\cdot\Psi^{\mathbf{B}}+\mathbf{d}\times\mathbf{B}\cdot\Psi^{\mathbf{d}\times\mathbf{B}}+\cdots+\boldsymbol{\mu}_I\cdot\Psi^{\mu_I} \qquad (75')$$

written so as to match the perturbed Hamiltonians (23), (25), and (45). From perturbation theory[10]

$$|\,\Psi^{\mathbf{B}}\rangle=-(e/2mc)\sum_j{}'\,|\,j\rangle\langle j\,|\,\mathbf{L}(\mathbf{r}')\,|\,0\rangle(E_j-E_0)^{-1} , \qquad (77)$$

$$|\,\Psi^{\mu_I}\rangle=-(e/mc)\sum_j{}'\,|\,j\rangle\langle j\,|\,\mathbf{M}_I\,|\,0\rangle(E_j-E_0)^{-1} , \qquad (78)$$

$$\begin{aligned} |\,\Psi^{\mathbf{d}\times\mathbf{B}}\rangle &= -(e/2mc)\sum_j{}'\,|\,j\rangle\langle j\,|\,\mathbf{P}\,|\,0\rangle(E_j-E_0)^{-1} \\ &= -\frac{ie}{2\hbar c}\mathbf{R}(\mathbf{r}')\Psi_0 , \end{aligned} \qquad (79)$$

where the last identity holds because of (75) and (76). One can introduce these quantities into the definition of the tensors (,) so that, for instance,

$$-\frac{e}{4mc}(\mathbf{P},\mathbf{L})_{-1}=\langle 0\,|\,\mathbf{P}\,|\,\Psi^{\mathbf{B}}\rangle=\langle 0\,|\,\mathbf{L}(\mathbf{r}')\,|\,\Psi^{\mathbf{d}\times\mathbf{B}}\rangle , \qquad (80)$$

$$-\frac{e}{2mc}(\mathbf{M}_I,\mathbf{P})_{-1}=\langle 0\,|\,\mathbf{M}_I\,|\,\Psi^{\mathbf{d}\times\mathbf{B}}\rangle=\langle 0\,|\,\mathbf{P}\,|\,\Psi^{\mu_I}\rangle . \qquad (81)$$

Both the probability density[5(b)]

$$P(\mathbf{r};\mathbf{s})=n\int d\mathbf{r}_2\cdots d\mathbf{r}_n\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n)\Psi^*(\mathbf{s},\mathbf{r}_2,\ldots,\mathbf{r}_n) , \qquad (82a)$$

$$P(\mathbf{r};\mathbf{r})\equiv P(\mathbf{r}) \qquad (82b)$$

and the n-electron current density[5(b)]

$$\mathbf{J}=-(e/m)\mathrm{Re}\{\boldsymbol{\pi}[P(\mathbf{r};\mathbf{s})]\}_{s=r} , \qquad (83a)$$

$$\boldsymbol{\pi}=\mathbf{p}+(e/2c)\mathbf{B}\times(\mathbf{r}-\mathbf{r}_0)+(e/c)\boldsymbol{\mu}_I\times\frac{\mathbf{r}-\mathbf{R}_I}{|\,\mathbf{r}-\mathbf{R}_I\,|^3} \qquad (83b)$$

can be expanded perturbatively according to (75′). We can isolate diamagnetic and paramagnetic terms of the current densities induced by the magnetic field and the nuclear dipole moment,

$$\mathbf{J}_d^B=-(e^2/2mc)\mathbf{B}\times\mathbf{r}P_0(\mathbf{r}) , \qquad (84)$$

$$\mathbf{J}_d^{\mathbf{r}_0\times\mathbf{B}}=-(e^2/2mc)\mathbf{r}_0\times\mathbf{B}P_0(\mathbf{r}) , \qquad (85)$$

TABLE I. Sum rules. Values are in atomic units; gauge origin is the fluorine nucleus. Coordinates: F (0,0,0); H (0,0,1.7328), also in a.u.

	STA	TDA	RPA
$(P_x,L_y)_{-1}$	0.828 86	0.867 13	0.962 57
$(P_x,K_y)_{-2}$	0.941 34	0.961 30	0.956 05
$(F_x,L_y)_{-2}$	0.486 40	0.142 01	0.903 17
$(F_x,K_y)_{-3}$	1.183 58	0.423 41	0.898 24
$\langle R_z\rangle$			0.975 23
$(P_x,M_{Fy})_{-1}$	0.511 53	1.996 85	0.233 73
$(F_x,M_{Fy})_{-2}$	−19.537 4	−21.353 1	−0.609 91
$\langle E_{Fz}\rangle$			0.325 20
$(P_x,M_{Hy})_{-1}$	−2.596 00	−2.611 30	−2.902 01
$(F_x,M_{Hy})_{-2}$	−2.383 60	−1.770 27	−2.828 56
$\langle E_{Hz}\rangle$			−3.014 24

$$\mathbf{J}_d^{\mu_I}=-(e^2/mc)\boldsymbol{\mu}_I\times\frac{\mathbf{r}-\mathbf{R}_I}{|\mathbf{r}-\mathbf{R}_I|^3}P_0(\mathbf{r})\ , \quad (86)$$

$$\mathbf{J}_p^{\mathbf{B}}=-(e/m)n\,\mathrm{Re}\int\{2\Psi_0^*(\mathbf{s},\mathbf{r}_2,\ldots,\mathbf{r}_n)\times\mathbf{p}[\mathbf{B}\cdot\boldsymbol{\Psi}^{\mathbf{B}}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n)]\times d\mathbf{r}_2\cdots d\mathbf{r}_n\}_{s=r}\ , \quad (87)$$

$$\mathbf{J}_p^{\mathbf{r}_0\times\mathbf{B}}=-(e/m)n\,\mathrm{Re}\int\{2\Psi_0^*(\mathbf{s},\mathbf{r}_2,\ldots,\mathbf{r}_n)\times\mathbf{p}[\mathbf{r}_0\times\mathbf{B}\cdot\boldsymbol{\Psi}^{d\times\mathbf{B}}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n)]\times d\mathbf{r}_2\cdots d\mathbf{r}_n\}_{s=r}\ , \quad (88)$$

$$\mathbf{J}_p^{\mu_I}=-(e/m)n\,\mathrm{Re}\int\{2\Psi_0^*(\mathbf{s},\mathbf{r}_2,\ldots,\mathbf{r}_n)\times\mathbf{p}[\boldsymbol{\mu}_I\cdot\boldsymbol{\Psi}^{\mu_I}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_n)]\times d\mathbf{r}_2\cdots d\mathbf{r}_n\}_{s=r}\ . \quad (89)$$

Then the integral condition for the conservation of the current density[15] $\int d\tau\,\mathbf{J}=0$ can be written, to first order in $\mathbf{B}$,

$$\int d\tau(\mathbf{J}_d^{\mathbf{B}}+\mathbf{J}_p^{\mathbf{B}})=(e^2/2m^2c)[\mathbf{B}\cdot(\mathbf{L},\mathbf{P})_{-1}-m\mathbf{B}\times\langle\mathbf{R}\rangle]=0\ , \quad (71'')$$

$$\int d\tau(\mathbf{J}_d^{\mathbf{r}_0\times\mathbf{B}}+\mathbf{J}_p^{\mathbf{r}_0\times\mathbf{B}})=(e^2/2m^2c)\mathbf{r}_0\times\mathbf{B}\cdot[(\mathbf{P},\mathbf{P})_{-1}-mn\mathbb{1}]=0\ , \quad (72'')$$

where $\langle\mathbf{R}\rangle=\langle 0|\mathbf{R}(0)|0\rangle$.

To first order in $\boldsymbol{\mu}_I$

TABLE II. Perpendicular components of the paramagnetic susceptibility in a.u. ppm, per molecule, gauge on fluorine. The conversion factor to usual cgs emu ppm is $8.923\,94\times10^{-2}$ cm^3 per mole. The speed of light in a.u. is 137.036. The theoretical diamagnetic susceptibilities are $\chi_\perp^d=-127.499$, $\chi_\parallel^d=-112.441$, $\chi_{\mathrm{av}}^d=-122.480$. The average susceptibility is -116.366. Reference 23 reports -115.4 ± 1, -116.

	L,L	K,L	K,K
STA	7.829	6.542	6.035
TDA	9.209	8.834	8.617
RPA	9.170	9.043	8.935

$$\int d\tau(\mathbf{J}_d^{\mu_I}+\mathbf{J}_p^{\mu_I})=(e^2/m^2c)\left[\boldsymbol{\mu}_I\cdot(\mathbf{M}_I,\mathbf{P})_{-1}-\frac{m}{c}\boldsymbol{\mu}_I\times\langle\mathbf{E}_I^n\rangle\right]=0\ . \quad (73'')$$

In addition we note that

$$\int d\tau\,\mathbf{J}=0=\left\langle\sum_{i=1}^{n}\pi_i\right\rangle \quad (90)$$

is a restatement of the hypervirial theorem for the operator $\mathbf{R}$ in the form of a momentum theorem.[16] Equations (71)–(73) establish the well-known connection between gauge invariance and current conservation.[16,17] Finally, we note that the mixed length-acceleration TRK sum rule (72) can be written

$$(\mathbf{R},\mathbf{F})_{-1}=\sum_{I=1}^{N}Z_I\gamma^I(0)\ ,$$
$$\gamma^I(0)=(2e/\hbar Z_I)\sum_j{}'\langle 0|\mathbf{E}_n^I|j\rangle\langle j|\mathbf{R}|0\rangle\omega_{j0}^{-1}\ , \quad (72''')$$

where the definition of static electric shielding of nucleus I, $\gamma^I(0)$, in the length gauge [see Eqs. (5) and (9) of Ref. 9(b)] has been used. This is an interesting connection between electric and magnetic properties in terms of a gauge-invariant condition.

VI. APPLICATION TO THE HF MOLECULE

The sum rules reported in Sec. V are rigorously valid for exact wave functions. However, owing to the results obtained by others in different contexts, they are also valid within the RPA-CHF methods[7,8,16] (provided that a complete set of expansion is adopted in the Hartree-Fock space), which makes these computational approaches very appealing. In actual calculations the sum rules (71)–(73) can be used to examine the degree of completeness of the

TABLE III. Perpendicular components of the paramagnetic shielding in ppm.

	$(2c^2)^{-1}(M_F,L)_{-1}$	$(2c^2)^{-1}(M_F,K)_{-2}$	$(2c^2)^{-1}(M_H,L)_{-1}$	$(2c^2)^{-1}(M_H,K)_{-2}$
STA	−53.299	−63.929	14.603	13.103
TDA	−101.419	−74.389	17.081	16.772
RPA	−102.760	−99.211	17.672	17.535

TABLE IV. Nuclear magnetic shielding in HF molecule. Angular momentum formalism. The entries within the parentheses specify the gauge origin. Experimental values from Refs. 20 and 22: $\sigma_{av}^{H}=29.2\pm0.5$, $\sigma_{av}^{F}=410\pm6$. $\sigma_{av}^{H}=28.8\pm0.5$ from Ref. 24.

		σ^d(F)	σ^p(F)	σ(F)	σ^d(H)	σ^p(H)	σ(H)
F	$\perp$	482.469	−102.760	379.709	467.465	−91.976	375.489
	$\parallel$	481.808	0.0	481.808	481.808	0.0	481.808
	av	482.249	−68.507	413.742	472.246	−61.317	410.929
H	$\perp$	1.629	17.672	19.301	140.697	−116.218	24.479
	$\parallel$	44.064	0.0	44.064	44.064	0.0	44.064
	av	15.774	11.781	27.555	108.486	−77.489	31.007

basis set with respect to various operators and to test the quality of approximate molecular wave functions.

We report here an extended study on the magnetic properties of the HF molecule, based on three different approximations to the Rowe's equations of motion (EOM),[2] namely, the single-transition approximation (STA), Tamm-Dancoff approximation (TDA), and RPA. A detailed description of the computational scheme adopted by us to solve the EOM equations, and information concerning the large CGTO basis of expansion (also retained in the present investigation) are available from a previous paper.[9(d)] In particular the excellent overall characteristics of our reference state for the HF molecule (an accurate SCF wave function) can be evinced by near-Hartree-Fock energy, polarizability, and nuclear electric shieldings in close agreement with experiment. The TRK sum rules obtained through the EOM calculations have already been reported to assess the high quality of the theoretical γ^I in Eq. (72‴): in RPA this is fulfilled to various degrees (from 96% to 99%).[9(d)] In the present context this is a first indication of the quality of the theoretical magnetic susceptibility reported in Table II.

The quantities entering the sum rules (71) and (73) are shown in Table I. As found previously,[9(d)] we can see that the STA and TDA estimates are usually poor. Good results are obtained in the RPA calculations, with the noticeable exception of the sum rule (73) for fluorine, as $(M_{Fy},F_x)_{-2}$ is 2 times larger than $\langle E_{Fz}\rangle$ and of wrong sign. As a matter of fact, properties and sum rules involving any operator $\mathbf{T}$ are obeyed, provided that $|j\rangle$ and $|\mathbf{T}j\rangle$ are both included in a truncated basis set $\{j\}$.[18] This sufficient condition is easily satisfied, adopting a CGTO basis of expansion, in length and linear and angular momentum gauges.[9] The operators **M**, **F**, and **K** are more difficult to represent because of the obvious difficulties to mimic their r^{-3} dependence using CGTO's, i.e., functions whose algebraic part contains only positive powers of r. Accordingly, the apparent failure observed in Table I indicates the deficiencies of our wave function in the environment of the heavy atom, evidenced by the severe test (73) in the torque formalism. This conclusion is also confirmed by the trend of sum rule (71), which deteriorates when force and torque operators are considered: $(\mathbf{K},\mathbf{F})_{-3}$ is, in fact, the less accurate one.

The theoretical paramagnetic susceptibilities are displayed in Table II. Within the RPA the three different formalisms give results that are in good agreement, which is a further indication of the accuracy of the calculation, and in excellent agreement with the best previous theoretical estimates.[19–22] The total theoretical magnetizability is −116.4 ppm a.u., matching with −116 quoted in Ref. 23. The equation for the average theoretical susceptibility[6] as a function of the distance from the fluorine atom, i.e., the origin of the gauge, is (all quantities in a.u.)

$$\chi_{av}(\mathbf{r})=-116.366+0.224\,579z -1.839\,523(x^2+y^2)-2.098\,635z^2 \ .$$

This indicates a high degree of gauge invariance.

The theoretical paramagnetic shieldings are reported in Table III. Both for fluorine and hydrogen the RPA results obtained in the K and L formalisms are virtually coincident with previous near-Hartree-Fock results.[19–22] As in the case of the electric properties,[9(d)] STA and TDA yield very poor paramagnetic properties (see Tables II and III) and must be considered unreliable theoretical tools in general. The theoretical magnetic shieldings within the L formalism are also reported in Table IV, corresponding to H and F as gauge origins. The total values, obtained for the different gauges, are very close in the case of fluorine, whereas a larger gauge variation, 4 ppm, is found for the hydrogen shielding. At any rate, a gratifying agreement with the experimental data has been found.

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