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Conditions for invariance of molecular magnetic properties in Landau
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General constraints for invariance of magnetic properties in a gauge transformation are analyzed. Sum
rules relative to the transformation from Coulomb to Landau gauges are examined in particular. Numerical
tests for hydrogen fluoride, water, ammonia, and methane molecule have been carried out in large basis set calculations, using random-phase approximation. The conditions for invariance are severe conditions for accuracy of variational molecular wave functions. © 1995 American Institute
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I. INTRODUCTION

The quality of an approximate variational wave function, describing a given electronic state of an atom or a molecule, can be assessed a priori, by checking the degree to which certain sum rules are satisfied, independently of any comparison between experimental data and corresponding quantities (i.e., electronic properties) estimated via the same wave function, which might be misleading in a number of cases. These sum rules are very general quantum mechanical relationships, fully obeyed by exact eigenfunctions to a model hamiltonian. They furnish “internal” yardsticks of accuracy as by-products of the main calculation.

In particular, the ability of a variational electronic wave function to predict accurate magnetic properties in a molecule is necessarily related to the degree of gauge dependence of these properties. This is a major physical requirement, as gauge invariance is connected to charge and current conservation in the presence of magnetic field via the continuity equation. Within the algebraic approximation, practicality of basis sets for determining theoretical magnetic properties can be estimated a priori, by checking their gauge invariance via proper sum rules.

In addition, a relevant theoretical question might be whether, if the approximate variational wave function is a good one, the gauge transformation also leads to a good approximate wave function. This question can be analyzed within the general framework of unitary invariance. If one uses the same set of trial functions \{\Psi\}, invariant to the action of a unitary operator \(U\) (which transforms a given function of the set \(\Psi \rightarrow U^{\dagger} \Psi\)) to solve the variational problem for both Hamiltonians \(H\) and \(H' = U^{\dagger} H U\), then the optimum variational energy stays the same, i.e., \(\hat{E} = \hat{E}\). In addition, the “best” variational wave function \(\Psi\) will have a series of physically desirable properties, in that it satisfies certain hypervirial theorems, i.e., the aforementioned sum rules.

In three previous papers, the Landau transformation of the vector potential in the Coulomb gauge has been investigated to obtain formulas for magnetic susceptibility and nuclear magnetic shieldings in a molecule in the presence of a static, time-independent, magnetic field. Quite remarkably, within the Landau gauge the diamagnetic contribution to susceptibility is a diagonal tensor, irrespective of coordinate system; besides, the diamagnetic contribution to nuclear shielding is fully described by a maximum of six independent components in the absence of molecular symmetry.

Numerical results demonstrate that very accurate electronic wave functions are necessary to obtain paramagnetic contributions to magnetic susceptibility of the same quality as those obtainable within the Coulomb gauge for vector potential. On the other hand, nuclear magnetic shielding tensors in the Landau gauge are characterized by the same quality as those evaluated in the Coulomb gauge. In addition to direct comparison of total magnetic properties within Coulomb and Landau gauges, the accuracy of theoretical estimates can be also checked by analyzing sum rules for origin independence of magnetic properties in a change of coordinate system, which can be described as a gauge transformation of the Landau vector potential. These topics have been recently reviewed.

The present paper is aimed at deriving, and checking via extended numerical tests, more general constraints for invariance of magnetic properties under a gauge transformation for a molecule in a static homogeneous magnetic field. Besides their theoretical interest, these sum rules, as previously emphasized, can be applied to test the characteristics of excellent basis sets for evaluating magnetic properties. In particular, the sum rules for gauge invariance studied in this paper are helpful to sample a basis set in different regions of the molecular domain, as they involve a series of peculiar operators, able to weigh different portions of charge distribution. Accordingly, an analysis of sum rules for gauge invariance might help understand the conditions under which the gauge transformed wave function is also a good candidate for describing properties of a given electronic state in a molecule.

In Sec. II the general case of an arbitrary gauge transformation is analyzed. Section III deals in particular with sum rules for invariance under a Landau transformation, and corresponding numerical results are discussed in Sec. IV. They lead to insights as to when the Landau gauge transformation will affect the accuracy of the approximations retained in a calculation of magnetic properties.
II. SUM RULES FOR INVARIANCE IN A GENERAL CHANGE OF GAUGE

Let us consider a molecule with \( n \) electrons, with mass \( m_e \), charge \(-e\), coordinates \( \mathbf{r}_i \), canonical momenta \( \mathbf{p}_i \), angular momenta \( \mathbf{I}_i = \mathbf{r}_i \times \mathbf{p}_i \), \( (i = 1, 2, \ldots, n) \), and \( N \) nuclei, with corresponding quantities \( \mathbf{M}_j \), \( \mathbf{Z}_j \mathbf{e}_j \), \( \mathbf{K}_j \), etc.

The “particle” Hamiltonian of the electrons is

\[
H^{(0)} = \sum_{i=1}^{n} \left( \frac{p_i^2}{2m_e} - \sum_{j 
eq i} \frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right) + \frac{1}{2} \sum_{j 
eq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|},
\]

with eigenstates \(|j\rangle\) and energy eigenvalues \( E_{(0)}^j \); the reference state is denoted by \(|a\rangle\) (the notation of previous papers\(^4\)–\(^6\) is retained here, e.g., \( L_a = \sum_{i=1}^{n} l_{i\alpha} \), \( \omega_{ja} = (1/\hbar)[E(0)_{a} - E(a)] \), etc.).

In the presence of a magnetic field \( \mathbf{B} \) with vector potential

\[
A^\alpha(r) = \frac{1}{\mathbf{e}} \times \mathbf{r}, \quad \nabla \cdot A^\alpha = 0,
\]

in the Coulomb gauge, the “interaction” Hamiltonian is

\[
V = \frac{e}{2m_e c} \sum_{i=1}^{n} (A^\alpha_i \cdot \mathbf{p}_i + \mathbf{p}_i \cdot A^\alpha_i) + \frac{e^2}{2m_e c^2} \sum_{i=1}^{n} A^\alpha_i \cdot A^\alpha_i,
\]

where \( A^\alpha_i = A^\alpha_i(r_i) \).

If a permanent magnetic dipole \( \mu_I \) on nucleus \( I \) is also present, with vector potential

\[
A^\mu_i(r) = -\mu_I \times \nabla \frac{1}{|\mathbf{r} - \mathbf{R}_i|},
\]

the interaction Hamiltonian (3) contains the additional terms

\[
\frac{e}{m_e c} \sum_{i=1}^{n} \mu_I A^\mu_i \cdot \mathbf{p}_i + \frac{e^2}{m_e c^2} \sum_{i=1}^{n} A^\alpha_i \cdot A^\mu_i.
\]

In a gauge transformation of the Coulomb vector potential,

\[
A^\alpha \rightarrow A'^\alpha = A^\alpha + \nabla \lambda,
\]

induced by the generating function \( \lambda \), the unitary operator acting on the electronic wave function is \( U = \exp\left\{-i(e\mathbf{e}/\hbar) \sum A^\alpha_i |\mathbf{r}_i| \right\} \). Both for exact eigenfunctions, and in the case of variational eigenfunctions belonging to a set of trial functions invariant to \( U \), the second-order energies,

\[
W^{BB} = -\frac{1}{2} \chi_{ab} B_a B_b = W_{d}^{BB} + W_{p}^{BB},
\]

\[
W^{\mu_B} = \mu_{Ia} \sigma^I_{ab} B_b = W_{d}^{\mu_B} + W_{p}^{\mu_B},
\]

are left invariant. This implies that a calculation of magnetic properties should fulfill constraints which can be expressed in the form of quantum mechanical sum rules. Denoting by

\[
\mathbf{A}(\mathbf{r}) = A^\alpha(\mathbf{r}) + A^\mu(\mathbf{r}),
\]

total vector potential at \( \mathbf{r} \), the contributions to second-order interaction energy can be written

\[
W_d^{BB} + W_d^{\mu_B} = e^2 \frac{e}{2m_e c^2} \left\langle \left[ \sum_{i=1}^{n} A_i^\alpha \cdot A_i^\alpha \right] a \right\rangle,
\]

\[
W_p^{BB} + W_p^{\mu_B} = -e^2 \frac{e^2}{2m_e c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \left\langle \left[ \sum_{i=1}^{n} (A_i^\alpha \cdot \mathbf{p}_i) \right] j \right\rangle \times \left\langle \left[ \sum_{i=1}^{n} (\nabla \lambda_i \cdot \mathbf{p}_i) \right] a \right\rangle.
\]

In a gauge transformation (6) the diamagnetic contributions transform

\[
W_d^{BB} \rightarrow W_d^{BB'} = W_d^{BB} + \Delta_d^{BB},
\]

\[
W_d^{\mu_B} \rightarrow W_d^{\mu_B'} = W_d^{\mu_B} + \Delta_d^{\mu_B},
\]

where

\[
W_d^{BB} = e^2 \frac{e}{2m_e c^2} \left\langle \left[ \sum_{i=1}^{n} A_i^\alpha \cdot A_i^\alpha \right] a \right\rangle,
\]

\[
\Delta_d^{BB} = e^2 \frac{e^2}{2m_e c^2 \hbar} \left\langle \left[ \sum_{j \neq a} \frac{2}{\omega_{ja}} (A_j^\alpha \cdot \mathbf{p}_i) \right] j \right\rangle \times \left\langle \left[ \sum_{i=1}^{n} (\nabla \lambda_i \cdot \mathbf{p}_i) \right] a \right\rangle,
\]

\[
W_d^{\mu_B} = e^2 \frac{e^2}{m_e c^2} \left\langle \left[ \sum_{i=1}^{n} A_i^\alpha \cdot A_i^\mu \right] a \right\rangle,
\]

\[
\Delta_d^{\mu_B} = e^2 \frac{e^2}{m_e c^2} \left\langle \left[ \sum_{j \neq a} \frac{2}{\omega_{ja}} (A_j^\alpha \cdot \mathbf{p}_i) \right] j \right\rangle \times \left\langle \left[ \sum_{i=1}^{n} (\nabla \lambda_i \cdot \mathbf{p}_i) \right] a \right\rangle.
\]
\[ W_{p}^{\mu\nu} = -\frac{e^2}{m_e^2c^2\hbar} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle \left( a \sum_{i=1}^{n} (A_{i}^{\mu\nu} \cdot p_{i}) \right) j \right\rangle \times \left\langle \left( j \sum_{i=1}^{n} (\nabla \lambda \cdot p_{i}) \right) a \right\rangle, \]  
\[ \Delta_{p}^{\mu\nu} = -\frac{e^2}{m_e^2c^2\hbar} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle \left( a \sum_{i=1}^{n} (A_{i}^{\mu\nu} \cdot p_{i}) \right) j \right\rangle \times \left\langle \left( j \sum_{i=1}^{n} (\nabla \lambda \cdot p_{i}) \right) a \right\rangle. \]  

Therefore, under a gauge transformation (6) of the Coulomb vector potential, general conditions for invariance of magnetic susceptibility are obtained via the identities

\[ \Delta_{p}^{BB} = -\Delta_{d}^{BB}, \Delta_{p}^{\mu\nu} = -\Delta_{d}^{\mu\nu}, \]  

in the form

\[ (A_{a}^{\gamma\alpha}p_{a}, \nabla_{a} \lambda p_{a} - 1 = m_{e} \left\langle a \sum_{i=1}^{n} (A_{i}^{\alpha\alpha} \nabla \alpha \lambda_{i}) a \right\rangle, \]  
\[ (\nabla_{a} \lambda p_{a}, \nabla_{a} \lambda p_{a} - 1 = m_{e} \left\langle a \sum_{i=1}^{n} (\nabla \lambda^{2})_{i} a \right\rangle, \]  
\[ (A_{a}^{\mu\alpha}p_{a}, \nabla_{a} \lambda p_{a} - 1 = m_{e} \left\langle a \sum_{i=1}^{n} (A_{i}^{\mu\alpha} \nabla \alpha \lambda_{i}) a \right\rangle, \]  

where

\[ (A_{a}^{\gamma\alpha}p_{a}, \nabla_{a} \lambda p_{a} - 1 = \frac{1}{h} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle a \sum_{i=1}^{n} (A_{i}^{\alpha\alpha} \nabla \alpha \lambda_{i}) j \right\rangle \times \left\langle j \sum_{i=1}^{n} (\nabla \lambda \nabla p_{i}) a \right\rangle, \]  
\[ (\nabla_{a} \lambda p_{a}, \nabla_{a} \lambda p_{a} - 1 = \frac{1}{h} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle a \sum_{i=1}^{n} (\nabla \lambda p_{i}) a \right\rangle \times \left\langle j \sum_{i=1}^{n} (\nabla_{a} \lambda \nabla p_{i}) j \right\rangle, \]  
\[ (A_{a}^{\mu\alpha}p_{a}, \nabla_{a} \lambda p_{a} - 1 = \frac{1}{h} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle a \sum_{i=1}^{n} (A_{i}^{\mu\alpha} \nabla \alpha \lambda_{i}) a \right\rangle \times \left\langle j \sum_{i=1}^{n} (\nabla \lambda \nabla p_{i}) a \right\rangle. \]  

The same formulas are established using the hypervirial theorem, via the off-diagonal relation

\[ \left\langle j \sum_{i=1}^{n} (\nabla \lambda \cdot p_{i}) a \right\rangle = im_{e} \omega_{ja} \left\langle j \sum_{i=1}^{n} \lambda_{i} a \right\rangle \]  
and the operator equations

\[ \frac{im_{e}}{\hbar} [H^{(0)}, \lambda] = \nabla \lambda \cdot p. \]  

These results can now be used to work out explicit conditions for invariance of molecular magnetic properties. The magnetic susceptibility tensor within the Coulomb gauge contains paramagnetic and diamagnetic contributions, compare for Eq. (7),

\[ \chi_{ab} = \chi_{ab}^{p} + \chi_{ab}^{d}, \]  
\[ \chi_{ab}^{p} = -\frac{e^2}{2m_e^2c^2\hbar} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle \left( a \sum_{i=1}^{n} (M_{i}^{a}g_{n}) \right) (j|L_{\beta}|a) \right\rangle, \]  
\[ \chi_{ab}^{d} = -\frac{e^2}{2m_e^2c^2} \left\langle a \sum_{i=1}^{n} (r_{ia}E_{ia} \delta_{ab} - r_{ia}E_{a}) a \right\rangle. \]  

Analogously the paramagnetic and diamagnetic contributions to magnetic shielding of nucleus I carrying the intrinsic moment, compare for Eq. (8), are

\[ \sigma_{I_{a}b}^{p} = \sigma_{I_{a}b}^{p} + \sigma_{I_{a}b}^{d}, \]  
\[ \sigma_{I_{a}b}^{p} = -\frac{e^2}{2m_e^2c^2\hbar} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle \left( a \sum_{i=1}^{n} (M_{i}^{a}g_{n}) \right) (j|L_{\beta}|a) \right\rangle, \]  
\[ \sigma_{I_{a}b}^{d} = -\frac{e^2}{2m_e^2c^2} \left\langle a \sum_{i=1}^{n} (r_{ia}E_{ia} \delta_{ab} - r_{ia}E_{a}) a \right\rangle. \]  

III. SUM RULES FOR INVARIANCE IN A LANDAU TRANSFORMATION

The Landau transformation is induced by the function

\[ \lambda^{\gamma \gamma} = \frac{1}{2} (B_{y}y \gamma + B_{z}z \gamma + B_{x}x \gamma), \]  
and the Landau vector potential, compare for Eq. (6), has components \( A_{x}^{\gamma} = A_{y}^{\gamma} = 0, A_{z}^{\gamma} = B_{x}, \) for a magnetic field in the z direction, \( B = e_{z}B_{z}, \) whereas \( A_{x}^{\gamma} = -\frac{1}{2}B_{y}, A_{y}^{\gamma} = \frac{1}{2}B_{x}, A_{z}^{\gamma} = 0. \) The magnetic properties, in this gauge, are written \( ^{d}g \)

\[ \chi_{xx}^{d} = -\frac{e^2}{m_e^2c^2} \left\langle a \sum_{i=1}^{n} \gamma_{i}^{2} a \right\rangle, \chi_{xy}^{d} = 0, \ldots, \]  
(\!
other tensor components are obtained by cyclic permutation of the indices x, y, and z). Off-diagonal diamagnetic components vanish for any coordinate system in the Landau gauge. The paramagnetic contribution is

\[ \chi_{xx}^{p} = \frac{e^2}{m_e^2c^2\hbar} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle a \sum_{i=1}^{n} (yp_{z})_{i} a \right\rangle \times \left\langle j \sum_{i=1}^{n} (yp_{z})_{i} a \right\rangle, \]  
\[ \chi_{xy}^{p} = \frac{e^2}{m_e^2c^2\hbar} \sum_{j>a} \frac{2}{\omega_{ja}} \left\langle a \sum_{i=1}^{n} (yp_{z})_{i} a \right\rangle \times \left\langle j \sum_{i=1}^{n} (zp_{z})_{i} a \right\rangle. \]  

The diamagnetic contribution to nuclear shielding is
The paramagnetic contribution is 

$$\sigma_{txy}^{\text{pl}} = -\frac{\epsilon}{m_0 c^2} \left( \frac{1}{a} \sum_{i=1}^{n} y_i E_{i_x} a \right),$$

and 

$$\sigma_{xy}^{\text{pl}} = -\frac{\epsilon}{m_0 c^2} \left( \frac{1}{a} \sum_{i=1}^{n} y_i E_{i_y} a \right),$$

etc. For any coordinate system, $\sigma_{txy}^{\text{pl}} = \sigma_{ytx}^{\text{pl}} = \sigma_{xty}^{\text{pl}} = 0$. The paramagnetic contribution is

$$\sigma_{txy} = \sigma_{xy} = \sigma_{xy} = 0,$$

etc. The conditions for invariance

$$X_{ab} = X_{ba},$$

$$\sigma_{ab} = \sigma_{ba},$$

imply, according to Eqs. (25)–(30), that the sum rules for susceptibilities,

$$(L_x, \mathcal{F}_{yz})_{-1} = \frac{m_e}{2} \left( \frac{1}{a} \sum_{i=1}^{n} (y_i^2 - z_i^2) a \right),$$

$$(L_x, \mathcal{F}_{zx})_{-1} + (L_y, \mathcal{F}_{yz})_{-1} = 0,$$

$$(\mathcal{F}_{yz}, \mathcal{F}_{yz})_{-1} = \frac{m_e}{4} \left( \frac{1}{a} \sum_{i=1}^{n} (y_i^2 + z_i^2) a \right),$$

$$(\mathcal{F}_{yz}, \mathcal{F}_{zx})_{-1} = \frac{m_e}{4} \left( \frac{1}{a} \sum_{i=1}^{n} (xy) a \right),$$

and for nuclear shielding,

$$(M_{i_x}^{\text{nu}}, \mathcal{F}_{yz})_{-1} = \frac{m_e}{2e} \left( \frac{1}{a} \sum_{i=1}^{n} (y_i E_{i_y} - z_i E_{i_z}) a \right),$$

$$(M_{i_x}^{\text{nu}}, \mathcal{F}_{zx})_{-1} = \frac{m_e}{2e} \left( \frac{1}{a} \sum_{i=1}^{n} x_i E_{i_x} a \right),$$

$$(M_{i_y}^{\text{nu}}, \mathcal{F}_{yz})_{-1} = -\frac{m_e}{2e} \left( \frac{1}{a} \sum_{i=1}^{n} y_i E_{i_y} a \right),$$

must be fulfilled (other tensor components are obtained by cyclic permutation of the indices $x$, $y$, and $z$). In these equations the off-diagonal hypervirial relation

$$\langle j | \mathcal{F}_{ab} | a \rangle = \frac{2}{m_0 c^2} \omega_{ja} \sum_{i=1}^{n} (r_a r_b) \langle a \rangle,$$

for the virial operator, compare for Refs. 1 and 10,

$$\mathcal{F}_{ab} = \frac{1}{2} \sum_{i=1}^{n} (r_a r_b + p_a r_b),$$

has been introduced (other symbols have the same meaning as in Refs. 4–6), so that, for instance

$$(L_x, \mathcal{F}_{yz})_{-1} = \frac{1}{2} \sum_{j=1}^{n} \omega_{ja} \left( \frac{1}{a} \sum_{i=1}^{n} (y_i E_{i_y} - z_i E_{i_z}) a \right),$$

etc. Sum rules for other components are obtained by cyclic permutations of the indices.

**IV. RESULTS AND DISCUSSION**

In previous papers magnetic properties have been evaluated ab initio for HF, H2O, NH3, and CH4 molecules, within the random-phase approximation (RPA), using Gaussian basis sets of increasing extension and flexibility.

The quality of theoretical magnetic susceptibilities and nuclear shieldings in the Landau gauge was established by direct comparison with corresponding quantities in the Coulomb gauge. Moreover, quite general yardsticks of accuracy for first-order perturbed wave functions, relying on Thomas–Reiche–Kuhn sum rules and other constraints for origin independence of theoretical magnetic properties, were used in extended numerical tests.

Much more specific criteria for assessing the overall quality of theoretical values in the Landau gauge is provided by Eqs. (47)–(50). According to these constraints, a given basis set should, at the same time, yield accurate representations of $\mathcal{F}_{ab}$, the virial operator (52), and of $M_{i_a}^{\text{nu}}$, the operator for the magnetic field of electrons on nucleus $I$. The former, defined via position and linear momentum, weighs the electron cloud in the tail regions of molecular domain, the latter, owing to $|r_i - R_i|^{-3}$ factor, samples charge distribution in the environment of the nuclei. It is quite difficult to meet both these requirements with a Gaussian basis set; “steep,” as well as diffuse polarization functions should be necessarily included. Therefore, results reported in Tables I–XV provide additional fairly complete information on the ability of electronic wave functions adopted in previous studies to predict magnetic properties within the Landau gauge.

For each molecule, four tables, showing theoretical estimates of sum rules (47), (49), and (50) respectively for hydrogen and heavy atom shieldings, are reported in the present study [for all the molecules of the series examined here constraint (48) is satisfied by symmetry]. For HF, NH3, and CH4, basis sets I–IV are the same as in Ref. 6. Similarly, for H2O, basis sets I–IV are those of Ref. 5. The same molecular geometries have been employed here.

Numerical results relative to sum rule (47) for susceptibility evaluated assuming the origin on a hydrogen nucleus, compare for Tables I, V, IX, and XIII demonstrate that basis sets of high quality are necessary to guarantee gauge invariance in a Landau transformation. Less accurate estimates were obtained for HF, where the discrepancies between left
and right-hand sides of Eq. (47) are ≈10%. On the other hand, the same constraint (47) is very accurately fulfilled for basis sets IV of NH3 and CH4, and almost exactly satisfied for basis set VI of H2O. This trend is confirmed by numerical tests for sum rule (49) (origin to hydrogen nucleus) involving two virial operators ~\( f_{\alpha \beta} \) compare for Tables II, VI, X and XIV. Possibly, an even more severe constraint for magnetic susceptibility of heavy atoms within the Coulomb gauge.4–6

A similar drawback is usually encountered in evaluating the \( M^\alpha_{\beta \gamma} \) tensor in analyzing origin dependence of nuclear magnetic shielding of heavy atoms within the Coulomb gauge.4–6 Accordingly, a possible explanation for this partial failure may be partially ascribed to lack of steep \( p \) functions in the basis sets retained for heavy atoms. In other words, in order to fulfill sum rule (50), one could add other sets of \( p \) Gaussian functions with high exponents to heavy nucleus basis, possibly forming an even tempered set.

### V. CONCLUSIONS

A series of sum rules for gauge invariance of electronic second-order energy terms in a Landau gauge transformation has been worked out. According to a well-known connection between gauge invariance and the continuity equation,2 the degree to which these constraints are fulfilled provides physical information on the reliability of a calculation of magnetic properties, i.e., charge and current conservation in the presence of magnetic field. These sum rules can be rewritten as hypervirial theorems,1 which hold exactly for operators involving two virial operators ~\( f_{\alpha \beta} \).

### TABLE I. Invariance condition (47) for magnetic susceptibility of the HF molecule.

| Basis set | \( 2(L_z, V_{zz})_i \) | \( \langle z^2 - x^2 \rangle \) |
|-----------|-----------------|-----------------|
| I         | −143.5          | 1856.4          |
| II        | −845.8          | 1536.1          |
| III       | −845.8          | 1912.3          |
| IV        | −143.5          | 1856.4          |

^In atomic units, a.u. Nonvanishing components evaluated with the origin on the hydrogen nucleus, \( (0.0,0.0,1.6455) \) bohr, \( (V_{zz})_i = (V_{zz}, V_{zz})_i \) and \( (V_{zz}, V_{zz})_i = (V_{zz}, V_{zz})_i = 0 \) by symmetry.

### TABLE II. Invariance condition (49) for magnetic susceptibility of the HF molecule.

| Basis set | \( 4(V_{zy}, V_{zy})_i \) | \( \langle x^2 + y^2 \rangle \) | \( 4(V_{yz}, V_{yz})_i \) | \( \langle z^2 + x^2 \rangle \) |
|-----------|-----------------|-----------------|-----------------|-----------------|
| I         | 120.8           | 4377.7          | 1536.3          | 1912.3          |
| II        | 143.5           | 4506.2          | 1741.4          | 1929.3          |
| III       | 384.5           | 449.8           | 1856.0          | 1929.2          |
| IV        | 385.0           | 450.1           | 1858.3          | 1929.5          |

^In atomic units, a.u. Nonvanishing components evaluated with the origin on the hydrogen nucleus, \( (0.0,0.0,1.6455) \) bohr, \( (V_{zy}, V_{zy})_i = (V_{zy}, V_{zy})_i \) and \( (V_{zy}, V_{zy})_i = (V_{zy}, V_{zy})_i = 0 \) by symmetry.

### TABLE III. Invariance condition (50) for nuclear magnetic shielding of hydrogen in the HF molecule.

| Basis set | \( 2(M^\alpha_{\beta \gamma})_i \) | \( \langle zE_z - xE_x \rangle \) |
|-----------|-----------------|-----------------|
| I         | 179.6           | 192.9           |
| II        | 206.7           | 193.1           |
| III       | 194.6           | 193.1           |
| IV        | 194.7           | 193.1           |

^Nonvanishing components evaluated with origin on hydrogen nucleus, \( (0.0,0.0,1.6455) \) bohr, \( (M^\alpha_{\beta \gamma})_i \) and \( (M^\alpha_{\beta \gamma})_i \) and \( (M^\alpha_{\beta \gamma})_i = 0 \) by symmetry.

### TABLE IV. Invariance condition (50) for nuclear magnetic shielding of fluorine in the HF molecule.

| Basis set | \( 2(M^\alpha_{\beta \gamma})_i \) | \( \langle zE_z - xE_x \rangle \) |
|-----------|-----------------|-----------------|
| I         | −61.6           | 0.2             |
| II        | −17.5           | 1.0             |
| III       | −3.0            | 1.2             |
| IV        | −10.0           | 1.2             |

^Nonvanishing components evaluated with origin on fluorine nucleus, \( (0.0, -0.08730) \) bohr, \( (M^\alpha_{\beta \gamma})_i \) and \( (M^\alpha_{\beta \gamma})_i \) and other components vanish by symmetry.
TABLE V. Invariance condition (47) for magnetic susceptibility of the H$_2$O molecule.$^a$

| Basis set | $2(L_{x}, V_{xy})_{1-1}$ | $(x^2-y^2)$ | $2(L_{x}, V_{xy})_{1-1}$ | $(z^2-x^2)$ | $2(L_{x}, V_{xy})_{1-1}$ | $(y^2-z^2)$ | $2(L_{x}, V_{xy})_{1-1}$ | $(yz)$ |
|-----------|--------------------------|-------------|--------------------------|-------------|--------------------------|-------------|--------------------------|-------|
| I         | 339.1                    | 394.9       | -164.5                   | -181.4      | -185.5                   | -213.5      | 214.3                    | 244.6 |
| II        | 311.9                    | 392.8       | -138.5                   | -182.0      | -179.1                   | -210.8      | 185.3                    | 245.4 |
| III       | 344.5                    | 391.6       | -171.5                   | -181.8      | -187.8                   | -209.8      | 224.7                    | 246.2 |
| IV        | 379.9                    | 392.4       | -180.5                   | -181.6      | -205.4                   | -210.8      | 238.8                    | 245.5 |
| V         | 385.1                    | 392.3       | -183.1                   | -181.3      | -208.0                   | -210.9      | 242.3                    | 245.4 |
| VI        | 390.2                    | 392.8       | -181.9                   | -182.1      | -209.3                   | -210.7      | 244.0                    | 245.4 |

$^a$In a.u. Nonvanishing components evaluated with origin on hydrogen nucleus, (0.1,431 53, -0.985 266) bohr, $(L_{x}, V_{xy})_{1-1} = (L_{x}, V_{xy})_{1-1} = 0$ by symmetry.

TABLE VI. Invariance condition (49) for magnetic susceptibility of the H$_2$O molecule.$^a$

| Basis set | $4(V_{xy}, V_{xy})_{1-1}$ | $(x^2+y^2)$ | $4(V_{xy}, V_{xy})_{1-1}$ | $(z^2+x^2)$ | $4(V_{xy}, V_{xy})_{1-1}$ | $(y^2+z^2)$ | $4(V_{xy}, V_{xy})_{1-1}$ | $(yz)$ |
|-----------|--------------------------|-------------|--------------------------|-------------|--------------------------|-------------|--------------------------|-------|
| I         | 1307.6                   | 1768.9      | 758.5                    | 1128.3      | 1964.6                   | 2313.0      | -341.7                   | -369.6 |
| II        | 1350.9                   | 1777.9      | 758.4                    | 1145.4      | 1901.0                   | 2232.9      | -287.1                   | -368.1 |
| III       | 1325.5                   | 1774.6      | 775.6                    | 1145.1      | 1980.4                   | 2320.0      | -356.2                   | -369.3 |
| IV        | 1595.1                   | 1775.7      | 895.8                    | 1143.3      | 2229.2                   | 2320.4      | -370.2                   | -368.2 |
| V         | 1632.4                   | 1777.0      | 919.8                    | 1144.2      | 2263.0                   | 2321.0      | -375.3                   | -368.0 |
| VI        | 1737.2                   | 1776.0      | 1095.1                   | 1143.8      | 2293.5                   | 2322.1      | -368.1                   | -368.0 |

$^a$In a.u. Nonvanishing components evaluated with origin on hydrogen nucleus, (0.1,431 53, -0.985 266) a.u., $(V_{xy}, V_{xy})_{1-1} = (V_{xy}, V_{xy})_{1-1} = 0$, $(xy) = (xz) = 0$ by symmetry.

TABLE VII. Invariance condition (50) for hydrogen magnetic shielding in the H$_2$O molecule.$^a$

| Basis set | $2(M_{Hx}, V_{yz})_{1-1}$ | $(x_{E_{x}}-y_{E_{z}})$ | $2(M_{Hx}, V_{yz})_{1-1}$ | $(z_{E_{x}}-x_{E_{z}})$ | $2(M_{Hx}, V_{yz})_{1-1}$ | $(y_{E_{z}}-z_{E_{z}})$ | $2(M_{Hx}, V_{yz})_{1-1}$ | $(z_{E_{z}})$ | $2(M_{Hx}, V_{yz})_{1-1}$ | $(y_{E_{z}})$ |
|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------|--------------------------|-------------|
| I         | -98.8                    | -109.0                   | 55.8                     | 58.9                     | 44.3                     | 50.1                     | -72.6                    | -78.5       | 78.1                     |
| II        | -78.8                    | -109.2                   | 42.7                     | 58.6                     | 35.7                     | 50.5                     | -54.3                    | -78.3       | 59.5                     |
| III       | -111.0                   | -109.1                   | 60.8                     | 58.5                     | 43.1                     | 50.6                     | -77.6                    | -78.5       | 86.0                     |
| IV        | -110.4                   | -109.2                   | 62.4                     | 58.7                     | 48.5                     | 50.6                     | -79.8                    | -78.4       | 87.2                     |
| V         | -112.9                   | -109.3                   | 63.9                     | 58.7                     | 49.5                     | 50.6                     | -82.3                    | -78.5       | 90.0                     |
| VI        | -111.0                   | -109.4                   | 60.1                     | 58.8                     | 50.6                     | 50.6                     | -79.8                    | -78.4       | 80.8                     |

$^a$Nonvanishing components evaluated with the origin on the hydrogen nucleus, (0.1,431 53, -0.985 266) bohr, $(y_{E_{z}}) = (z_{E_{z}})$, $(M_{Hx}^0, V_{yz})_{1-1} = (M_{Hx}^0, V_{yz})_{1-1} = (M_{Hx}^0, V_{yz})_{1-1} = (M_{Hx}^0, V_{yz})_{1-1} = 0$ by symmetry. In the HF limit $2(M_{Hx}^0, V_{yz})_{1-1} = (y_{E_{z}}) = -2(M_{Hx}^0, V_{yz})_{1-1}$.

TABLE VIII. Invariance condition (50) for oxygen magnetic shielding in the H$_2$O molecule.$^a$

| Basis set | $2(M_{Ox}, V_{yz})_{1-1}$ | $(x_{E_{x}}-y_{E_{z}})$ | $2(M_{Ox}, V_{yz})_{1-1}$ | $(z_{E_{x}}-x_{E_{z}})$ | $2(M_{Ox}, V_{yz})_{1-1}$ | $(y_{E_{z}}-z_{E_{z}})$ | $2(M_{Ox}, V_{yz})_{1-1}$ | $(z_{E_{z}})$ | $2(M_{Ox}, V_{yz})_{1-1}$ | $(y_{E_{z}})$ |
|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-------------|--------------------------|-------------|
| I         | 19.1                     | -2.8                     | -32.4                    | 2.2                      | -23.3                    | 0.6                      |                        |             |                          |
| II        | -24.5                    | -3.6                     | 25.0                     | 2.6                      | -8.8                     | 1.0                      |                        |             |                          |
| III       | -55.8                    | -3.1                     | 58.0                     | 2.2                      | 21.6                     | 0.9                      |                        |             |                          |
| IV        | 3.5                      | -3.8                     | 22.0                     | 2.7                      | -5.6                     | 1.1                      |                        |             |                          |
| V         | 18.4                     | -3.8                     | 4.7                      | 2.7                      | -6.2                     | 1.1                      |                        |             |                          |
| VI        | 5.2                      | -4.1                     | -2.9                     | 3.1                      | -1.8                     | 1.1                      |                        |             |                          |

$^a$Nonvanishing components evaluated with the origin on the oxygen nucleus, (0.0,0.124 144) bohr, $(y_{E_{z}}) = (z_{E_{z}}) = (x_{E_{z}}) = (y_{E_{z}}) = (z_{E_{z}}) = 0$, $(M_{Ox}^0, V_{yz})_{1-1} = (M_{Ox}^0, V_{yz})_{1-1} = (M_{Ox}^0, V_{yz})_{1-1} = (M_{Ox}^0, V_{yz})_{1-1} = 0$ by symmetry. In the HF limit $2(M_{Ox}^0, V_{yz})_{1-1} = (y_{E_{z}}) = -2(M_{Ox}^0, V_{yz})_{1-1}$.
TABLE IX. Invariance condition (47) for magnetic susceptibility of the NH₃ molecule.*

| Basis set | \(2(L_x, V_{xy})_{-1}\) | \((x^2 - y^2)\) | \(2(L_x, V_{xz})_{-1}\) | \((z^2 - x^2)\) | \(2(L_x, V_{yz})_{-1}\) | \((y^2 - z^2)\) | \(2(L_x, V_{yx})_{-1}\) | \((xz)\) |
|-----------|----------------|-------------|----------------|-------------|----------------|-------------|----------------|-------------|
| I         | −517.1        | −556.7      | 465.0          | 527.9       | 34.5           | 28.8        | 168.4          | 177.7       |
| II        | −556.0        | −556.7      | 511.6          | 523.9       | 36.1           | 32.9        | 178.2          | 178.4       |
| III       | −555.9        | −556.7      | 515.0          | 524.0       | 34.3           | 32.8        | 178.3          | 178.3       |
| IV        | −554.7        | −556.7      | 519.6          | 524.3       | 32.7           | 32.4        | 177.9          | 178.4       |

*In a.u. Nonvanishing components evaluated with origin on hydrogen nucleus, \((-0.885 \ 50.1.533 \ 73. -0.591 \ 96)\) bohr, \((L_x, V_{xy})_{-1}= (L_x, V_{yx})_{-1}=0\), \((xy)=0\) by symmetry.

TABLE X. Invariance condition (49) for magnetic susceptibility of the NH₃ molecule.*

| Basis set | \(4(V_{xy}, V_{yz})_{-1}\) | \((x^2 + y^2)\) | \(4(V_{xz}, V_{yz})_{-1}\) | \((z^2 + x^2)\) | \(4(V_{xz}, V_{yz})_{-1}\) | \((y^2 + z^2)\) | \(4(V_{yz}, V_{yz})_{-1}\) | \((xz)\) |
|-----------|----------------|-------------|----------------|-------------|----------------|-------------|----------------|-------------|
| I         | 2333.6        | 2658.2      | 2291.6         | 2744.5      | 793.0          | 1074.3      | 236.2          | 266.6       |
| II        | 2561.2        | 2661.8      | 2582.1         | 2760.4      | 939.0          | 1090.2      | 265.8          | 267.5       |
| III       | 2599.1        | 2662.6      | 2643.5         | 2760.9      | 995.4          | 1090.7      | 266.8          | 267.5       |
| IV        | 2633.8        | 2663.3      | 2714.5         | 2760.5      | 1057.7         | 1090.3      | 267.3          | 267.6       |

*In a.u. Nonvanishing components evaluated with the origin on hydrogen nucleus, \((-1.771 \ 00.0.0.0. -0.591 \ 96)\) bohr, \((V_{yz}, V_{yz})_{-1}= (V_{xz}, V_{yz})_{-1}=0\), \((xy)=0\) by symmetry.

TABLE XI. Invariance condition (50) for hydrogen magnetic shielding in the NH₃ molecule.*

| Basis set | \(2(M_{xx}^H, V_{xy})_{-1}\) | \((xE_x - yE_y)\) | \(2(M_{yy}^H, V_{xz})_{-1}\) | \((E_x - zE_z)\) | \(2(M_{zz}^H, V_{yz})_{-1}\) | \((yE_y - zE_z)\) | \(2(M_{yz}^H, V_{yz})_{-1}\) | \((zE_z - xE_x)\) |
|-----------|----------------|-------------|----------------|-------------|----------------|-------------|----------------|-------------|
| I         | 118.1          | −100.2      | −108.0         | −18.0       | −15.8          | 43.4        | 45.5           | −47.4       |
| II        | 127.9          | −124.0      | −109.1         | −108.4      | −17.1          | 15.6        | 45.3           | −48.9       |
| III       | 128.2          | −124.0      | −109.5         | −108.4      | −17.1          | 15.6        | 46.1           | −48.6       |
| IV        | 125.8          | −123.9      | −108.9         | −108.4      | −16.0          | 15.5        | 45.8           | −46.4       |

*Nonvanishing components evaluated with origin on hydrogen nucleus, \((-1.771 \ 00.0.0.0. -0.591 \ 96)\) a.u., \((M_{yy}^H, V_{yz})_{-1}=(M_{xx}^H, V_{xy})_{-1}=(M_{zz}^H, V_{yz})_{-1}=0\) by symmetry. In the HF limit \(2(M_{xx}^H, V_{xy})_{-1}=(xE_x)=(zE_z)=-2(M_{yz}^H, V_{yz})_{-1}\).

TABLE XII. Invariance condition (50) for nitrogen magnetic shielding in the NH₃ molecule.*

| Basis set | \(2(M_{xx}^N, V_{xz})_{-1}\) | \((xE_x - zE_z)\) | \(2(M_{yy}^N, V_{yz})_{-1}\) | \((yE_y - zE_z)\) | \(2(M_{zz}^N, V_{yz})_{-1}\) | \((zE_z - xE_x)\) |
|-----------|----------------|-------------|----------------|-------------|----------------|-------------|
| I         | 28.4           | −3.7        | −28.4          | 3.7         | −9.2           | 0.0         |
| II        | −1.1           | −4.4        | 1.1            | 4.4         | −2.3           | 0.0         |
| III       | 2.9            | −4.4        | −2.9           | 4.4         | 0.2            | 0.0         |
| IV        | 0.2            | −4.6        | −0.1           | 4.6         | 0.4            | 0.0         |

*Nonvanishing components evaluated with origin on nitrogen nucleus, \((0.0.0.127 \ 80)\) bohr, \(2(M_{yy}^N, V_{yz})_{-1}=-0.01\), only for basis set IV.

TABLE XIII. Invariance condition (47) for magnetic susceptibility in the CH₄ molecule.*

| Basis set | \(2(L_x, V_{xy})_{-1}\) | \((x^2 - y^2)\) | \(2(L_x, V_{xz})_{-1}\) | \((z^2 - x^2)\) | \(2(L_x, V_{yz})_{-1}\) | \((y^2 - z^2)\) |
|-----------|----------------|-------------|----------------|-------------|----------------|-------------|
| I         | 466.6          | 503.0       | −239.2         | −251.5      | −330.0         | −355.7       |
| II        | 499.4          | 503.0       | −252.8         | −251.5      | −353.1         | −355.7       |
| III       | 500.7          | 503.0       | −253.5         | −251.5      | −354.1         | −355.7       |
| IV        | 501.7          | 503.0       | −251.5         | −251.5      | −354.7         | −355.7       |

*In a.u. Nonvanishing components evaluated with the origin on hydrogen nucleus, \((0.1.683 \ 396.1.190 \ 341)\) bohr, \((L_x, V_{xy})_{-1}=(L_x, V_{yz})_{-1}=0\), \((xy)=(xz)=0\) by symmetry.
TABLE XIV. Invariance condition (49) for magnetic susceptibility of the CH₄ molecule.

| Basis set | 4(Vₓₓ, Vᵧᵧ) −1 | (x² + y²) | 4(Vₓᵧ, Vᵧₓ) −1 | (z² + x²) | 4(Vᵧᵧ, Vₓₓ) −1 | (y² + z²) | 4(Vₓᵧ, Vᵧₓ) −1 | (y₂ + z₂) |
|-----------|----------------|-----------|----------------|-----------|----------------|-----------|----------------|-----------|
| I         | 2501.0         | 2774.7    | 1826.4         | 2020.2    | 3155.9         | 3529.2    | 507.4          | 533.5     |
| II        | 2682.2         | 2779.4    | 1929.0         | 2049.4    | 3397.2         | 3533.9    | 536.3          | 533.5     |
| III       | 2686.1         | 2779.3    | 1931.7         | 2024.8    | 3395.8         | 3533.9    | 537.8          | 533.5     |
| IV        | 2747.3         | 2779.3    | 2002.8         | 2024.8    | 3499.8         | 3533.8    | 533.5          | 533.5     |

*Nonvanishing components evaluated with the origin on hydrogen nucleus. (0, 1.683 396 3.1.190 340 9) a.u. (Vₓₓ, Vᵧᵧ) = (Vᵧᵧ, Vₓₓ) = 0, (xy) = (xz) by symmetry.

TABLE XV. Invariance condition (50) for hydrogen magnetic shielding in the CH₄ molecule.

| Basis set | 2(Mₓₓ, Vₓᵧ) −1 | ⟨xEₓ − yEᵧ⟩ | 2(Mᵧᵧ, Vₓᵧ) −1 | ⟨zEₓ − xEᵧ⟩ | 2(Mᵧᵧ, Vᵧᵧ) −1 | ⟨yEᵧ − zEᵧ⟩ | 2(Mₓₓ, Vᵧᵧ) −1 | ⟨yEₓ⟩ |
|-----------|----------------|-----------|----------------|-----------|----------------|-----------|----------------|-----------|
| I         | −74.3          | −79.2     | 38.0           | 39.6      | 38.0           | 39.6      | 52.5           | 56.0      |
| II        | −79.8          | −79.3     | 40.3           | 39.6      | 40.3           | 39.6      | 56.5           | 56.0      |
| III       | −80.3          | −79.3     | 40.5           | 39.6      | 40.5           | 39.6      | 56.7           | 56.0      |
| IV        | −79.7          | −79.3     | 39.8           | 39.6      | 39.8           | 39.6      | 56.4           | 56.0      |

*Nonvanishing components evaluated with the origin on hydrogen nucleus. (0, 1.683 396 3.1.190 340 9) a.u., (Vₓₓ, Vᵧᵧ) = (Vᵧᵧ, Vₓₓ) = 0 by symmetry; 2(Mₓₓ, Vₓᵧ) −1 = (⟨yEₓ⟩ + ⟨zEᵧ⟩) = 0 in the HF limit.

That is to be fulfilled to guarantee that, starting from an accurate wave function, the gauge transformed wave function is also a good one.

Extended Gaussian basis sets have been adopted for HF, H₂O, NH₃, and CH₄ molecules. The calculations show that the sum rules examined in this work yield extremely severe tests of accuracy for SCF wave functions; the basis set must contain diffuse polarization functions to satisfy constraints (47)–(49) (see text), i.e., an accurate representation of the virial tensor operator should be provided to ensure invariant magnetic susceptibilities.

This requirement is comparably easier to fulfill than that necessary for invariance of magnetic shielding, compare for sum rules (50). In this case, in addition to guaranteeing a reliable representation of the virial operator, the basis set for heavy nuclei must also be enriched with steep polarization functions to accurately represent the operator for magnetic field of electrons on the nucleus in question.

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