Some mathematical properties of gauge transformations with respect to the Coulomb's gauge: variational analysis of an energy functional

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Abstract

As gauge invariance of computed magnetic properties, usually partitioned into diamagnetic and paramagnetic terms, is not achieved within the algebraic approximation, unless *ad hoc* techniques are adopted, a general variational treatment is analyzed, attempting to minimize the term more difficult to evaluate accurately, i.e., the paramagnetic contribution to magnetic susceptibility, by means of a gauge transformation. It is shown that an absolute minimum in a variational sense cannot be determined a priori. However, a 'local' minimum of the paramagnetic contribution to magnetic susceptibility can be arrived at by employing general gauge transformations of polynomial form.

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I Introduction

The gauge problem affecting theoretical evaluation of response properties of a molecule in the presence of an external magnetic field arises from the unphysical dependence of calculated values on the non-unique definition of the vector potential.

It is well-established, from theoretical [1, 2], as well as computational point of view [3, 4], that coupled Hartree-Fock (CHF) methods [1] yield magnetic susceptibility and nuclear magnetic shielding invariant to a gauge transformation only in the limit of complete atomic basis sets. This requirement brings in serious difficulties, for, in most cases, use of large basis sets is mandatory to achieve near Hartree-Fock accuracy, and, at the same time, a satisfactory degree of gauge independence.

Several computational procedures have been proposed so far to circumvent the problem of gauge translation, and related invariance of calculated magnetic properties in a change of coordinate system. Current methods exploit atomic basis sets explicitly depending on a gauge factor (GIAO) [5], individual gauges for localized molecular orbitals (IGLO) [6], and (LORG) [7].

Theoretical determinations of magnetic properties of a molecule perturbed by an external magnetic field, assumed, for the sake of simplicity, spatially uniform and time independent, are usually obtained by retaining the Coulomb gauge for the vector potential $\mathbf{A}^{\mathcal{C}}$ [8]:

$$\mathbf{A}^{\mathcal{C}}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}, \qquad \nabla \cdot \mathbf{A}^{\mathcal{C}} = 0. \tag{1}$$

The flux of the external magnetic field $\mathbf{B} = \nabla \times \mathbf{A}^{\mathcal{C}}$ is obviously invariant in a gauge transformation [8]

$$\mathbf{A}^{\mathcal{C}} \to \mathbf{A}^{\mathcal{C}} + \nabla\Lambda, \tag{2}$$

where $\Lambda(\mathbf{r})$ is an arbitary function of position, well behaved for $r \to \infty$. When a gauge transformation is carried out, the wave function ψ and the Hamiltonian h of a particle with charge q are transformed according to the equations

$$\psi \to \psi' = \psi \exp\left(\frac{iq}{\hbar c}\Lambda\right) \qquad h \to h' = \exp\left(\frac{iq}{\hbar c}\Lambda\right) h \exp\left(-\frac{iq}{\hbar c}\Lambda\right), \tag{3}$$

leaving invariant the one particle Schrödinger equation $h\psi = \epsilon\psi$. If the basis set is complete, also the calculated energy of the system is gauge-invariant, and the electronic current density is conserved, i.e., $\nabla \cdot \mathbf{j} = 0$ [2]. For wavefunctions that are exact eigenfunctions to some model hamiltonian, the choice of gauge is immaterial, because variations of the diamagnetic and paramagnetic contributions arising from a change of gauge cancel out one another, leaving invariant total magnetic properties. More generally, in the case of actual calculations relying on the algebraic approximation, selecting a gauge, e.g., specifying the "best" form of the vector potential, introduces serious problems: the fulfillment of constraints for gauge invariance constitutes a severe test of reliability for the computational scheme, and a hallmark of quality of the molecular wave function.

The gauge transformations which received most attention so far are usually related to a change of origin of coordinate system, $\mathbf{r}' \to \mathbf{r}'' = \mathbf{r}' + \mathbf{d}$, with $\mathbf{d}$ an arbitrary vector. They are limited to a class of Λ functions such that

$$\mathbf{A}^{\mathcal{C}''} = \mathbf{A}^{\mathcal{C}'} + \nabla\Lambda, \qquad \Lambda \equiv \mathbf{d} \cdot \mathbf{A}^{\mathcal{C}'}, \qquad \mathbf{A}^{\mathcal{C}'} = \mathbf{A}^{\mathcal{C}}(\mathbf{r} - \mathbf{r}'). \tag{4}$$

More general gauge transformations have been also proposed. The Landau gauge [8] for computing magnetic properties was studied in a series of articles [9]-[12].

Within Coulomb and Landau gauges, the vector potential is purely transverse; an alternative form of vector potential containing a longitudinal component has also been considered [13]. Some interesting features of these gauges were pointed out elsewhere [9]- [13].

Besides the mere theoretical interest, the use of Landau and longitudinal gauges is characterized by some remarkable features in numerical applications, as they provide clear-cut intrinsic criteria for assessing the accuracy of a calculation a priori, e.g., these alternative gauges furnish the tools for estimating Hartree-Fock limits to magnetic properties.

Chan and Das [14] have shown that, within the Coulomb gauge, the paramagnetic contribution to susceptibility reaches a minimum when the origin of the vector potential is fixed in the electronic centroid. Sadlej [15] suggested another scheme for choosing the optimal gauge origin in a finite basis set calculation of magnetic properties, by minimizing the basis set errors affecting computed second-order energy, and proved that the best gauge origin may not coincide with the electronic centroid. He took into account completeness criteria for a given basis set in calculating molecular magnetic properties. The advantage of this scheme over that of Chan and Das is that the latter does not provide any criterion for the gauge origin in the case of nuclear magnetic shielding constants.

For a given molecule, and for the same coordinate origin, the paramagnetic contribution to magnetic susceptibility evaluated within Landau and longitudinal gauges is systematically larger than Coulomb's, (which suggests that Coulomb gauge should preferably be used in actual calculations, *vide infra*). Therefore the question naturally arises whether another gauge may be adopted, such that the paramagnetic contribution to susceptibility becomes smaller than Coulomb's. Accordingly, the present work is aimed at investigating whether it is formally possible to choose a special form of the vector potential such that, allowing for the customary partition of magnetic susceptibility into diamagnetic and paramagnetic contributions, the latter is an absolute minimum. The interest of such a gauge, if it were available, is evident, since it would imply that total magnetic susceptibility can be calculated with higher precision. In fact, the diamagnetic term is an expectation value over the reference state, which is usually calculated with great accuracy, whereas a satisfactory description of excited states, needed to evaluate the paramagnetic contribution, is much more difficult to obtain.

In the present article the general physical requirement of gauge invariance of molecular magnetic properties is tackled by a variational approach, by considering a complete set of trial gauge transformations, $\{\Lambda_i\}$, in order to check if a minimum of the paramagnetic contribution to the exact magnetic susceptibility can be formally attained by using one of these generating functions. A two-terms functional, suitable to analyze the properties of a molecule in the presence of an external magnetic field is studied. The first term of this functional is related to the paramagnetic contribution to the interaction energy within the Coulomb gauge for the vector potential.

A gauge transformation is taken into account via the second term, defined by a generating Λ function well behaved for $r \to \infty$. If there existed a scalar function Λ giving rise to a maximum of the functional, then the corresponding Λ would be a critical point for the proposed functional, and a solution of the Euler-Lagrange equations. By employing a formal procedure, it is proven that the paramagnetic contribution to magnetic susceptibility cannot go through an absolute minimum in the variational sense.

Sec. II of this paper deals with general invariance conditions to be fulfilled for the exact eigenfunction of a model Hamiltonian. In Sec. III it is proven that an extremum of the functional cannot be determined, whereas a local minimum can be found. Such a local minimum is determined in Sec. IV for some small molecules.

II Invariance conditions 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 $\mathbf{p}_i$, $(i = 1, 2, ..., n)$, and N nuclei, with corresponding quantities M_I, $Z_I e$, $\mathbf{R}_I$, etc..

The "particle" electronic Hamiltonian is

$$H^{(0)} = \sum_{i=1}^{n} \left[\frac{{p_i}^2}{2m_e} - \sum_{I=1}^{N} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{j \neq i}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] + \frac{1}{2} \sum_{I}^{N} \sum_{J \neq I}^{N} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}, \tag{5}$$

with eigenstates $\left|\Psi_j^{(0)}\right\rangle \equiv |j\rangle$ and energy eigenvalues $E_j^{(0)}$; the reference state is denoted by $\left|\Psi_a^{(0)}\right\rangle \equiv |a\rangle$ (the notation of previous papers [9] is retained throughout this article, e.g., $\omega_{ja} = (E_j^{(0)} - E_a^{(0)})/\hbar$, etc.). In the presence of a magnetic field $\mathbf{B}$ with vector potential (1) in the Coulomb gauge, the "interaction" Hamiltonian is

$$V = \frac{e}{m_e c} \sum_{i=1}^{n} \mathbf{A}_i^{\mathcal{C}} \cdot \mathbf{p}_i + \frac{e^2}{2m_e c^2} \sum_{i=1}^{n} \mathbf{A}_i^{\mathcal{C}} \cdot \mathbf{A}_i^{\mathcal{C}}. \tag{6}$$

If a permanent dipole μ_I on nucleus I is also present, with vector potential

$$\mathbf{A}^{\mu_I}(\mathbf{r}) = \mu_I \times \frac{\mathbf{r} - \mathbf{R}_I}{|\mathbf{r} - \mathbf{R}_I|}, \tag{7}$$

the interaction Hamiltonian (6) contains the additional terms

$$\frac{e}{m_e c} \sum_{i=1}^{n} \mathbf{A}_i^{\mu_I} \cdot \mathbf{p}_i + \frac{e^2}{m_e c} \sum_{i=1}^{n} \mathbf{A}_i^{\mathcal{C}} \cdot \mathbf{A}_i^{\mu_I}. \tag{8}$$

The second-order energy expression contains two terms,

$$W^{BB} = -\frac{1}{2} \left(\chi_{\alpha\beta}^{\mathrm{d}} + \chi_{\alpha\beta}^{\mathrm{p}} \right) B_\alpha B_\beta = W_d^{BB} + W_p^{BB}, \tag{9}$$

$$W^{\mu_I B} = \mu_{I\alpha} \left(\sigma_{\alpha\beta}^{\mathrm{d}I} + \sigma_{\alpha\beta}^{\mathrm{p}I} \right) B_\beta = W_d^{\mu_I B} + W_p^{\mu_I B}, \tag{10}$$

where $\chi_{\alpha\beta}$ and $\sigma_{\alpha\beta}^I$ are the cartesian components of magnetic susceptibility and magnetic shielding of nucleus I, which are to be invariant in the gauge transformation (2). These second-order contributions can also be written

$$W_d^{BB} + W_d^{\mu_I B} = \frac{e^2}{2m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \mathbf{A}_i \cdot \mathbf{A}_i \right| a \right\rangle \tag{11}$$

$$W_p^{BB} + W_p^{\mu_I B} = -\frac{e^2}{m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{1}{\omega_{ja}} \operatorname{Re} \left(\left\langle a \left| \sum_{i=1}^{n} (A_\alpha p_\alpha)_i \right| j \right\rangle \left\langle j \left| \sum_{i=1}^{n} (A_\beta p_\beta)_i \right| a \right\rangle \right) \tag{12}$$

denoting by

$$\mathbf{A}(\mathbf{r}) = \mathbf{A}^{\mathcal{C}}(\mathbf{r}) + \mathbf{A}^{\mu_I}(\mathbf{r}) \tag{13}$$

the total vector potential at $\mathbf{r}$. Repeated Greek indices in tensor equations imply summation over x, y, and z throughout this paper.

In a gauge transformation the contributions which define the magnetic susceptibility tensor transform according to the expressions

$$W_d^{BB} \rightarrow W_d^{\prime BB} = W_d^{BB} + \Delta_d^{BB}, \tag{14}$$

$$W_p^{BB} \rightarrow W_p^{\prime BB} = W_p^{BB} + \Delta_p^{BB} \tag{15}$$

where

$$W_d^{BB} = \frac{e^2}{2m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \left(A_\alpha^{\mathcal{C}} A_\alpha^{\mathcal{C}} \right)_i \right| a \right\rangle, \tag{16}$$

$$\Delta_d^{BB} = \frac{e^2}{2m_e c^2}\left[2\left\langle a\left|\sum_{i=1}^{n}\left(\mathbf{A}^{\mathcal{C}}\cdot\nabla\Lambda\right)_i\right|a\right\rangle + \left\langle a\left|\sum_{i=1}^{n}\left(\nabla\Lambda\right)_i^2\right|a\right\rangle\right]. \tag{17}$$

$$W_p^{BB} = -\frac{e^2}{m_e^2 c^2 \hbar}\sum_{j\neq a}\frac{1}{\omega_{ja}}\,\mathrm{Re}\left(\left\langle a\left|\sum_{i=1}^{n}\left(A_\alpha^{\mathcal{C}}p_\alpha\right)_i\right|j\right\rangle\left\langle j\left|\sum_{i=1}^{n}\left(A_\beta^{\mathcal{C}}p_\beta\right)_i\right|a\right\rangle\right), \tag{18}$$

$$\begin{aligned}\Delta_p^{BB} \;=\; & -\frac{e^2}{2m_e^2c^2\hbar}\left[2\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left(\left\langle a\left|\sum_{i=1}^{n}(A_\alpha^{\mathcal{C}}p_\alpha)_i\right|j\right\rangle\left\langle j\left|\sum_{i=1}^{n}\left(\nabla_\beta\Lambda p_\beta\right)_i\right|a\right\rangle\right)\right.\\ & \left.+\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left(\left\langle a\left|\sum_{i=1}^{n}\left(\nabla_\alpha\Lambda p_\alpha\right)_i\right|j\right\rangle\left\langle j\left|\sum_{i=1}^{n}\left(\nabla_\beta\Lambda p_\beta\right)_i\right|a\right\rangle\right)\right].\end{aligned} \tag{19}$$

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

$$\Delta_p^{BB} = -\Delta_d^{BB} \tag{20}$$

in the form

$$\left(A_\alpha^C p_\alpha, \nabla_\beta\Lambda p_\beta\right)_{-1} = m_e\left\langle a\left|\sum_{i=1}^{n}\left(A_\alpha^{\mathcal{C}}\nabla_\alpha\Lambda\right)_i\right|a\right\rangle, \tag{21}$$

$$\left(\nabla_\alpha\Lambda p_\alpha, \nabla_\beta\Lambda p_\beta\right)_{-1} = m_e\left\langle a\left|\sum_{i=1}^{n}\left(\nabla\Lambda\right)_i^2\right|a\right\rangle, \tag{22}$$

where the definitions

$$\begin{aligned}&\left(A_\alpha^C p_\alpha, \nabla_\beta\Lambda p_\beta\right)_{-1}\\ &\quad=\frac{1}{\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left(\left\langle a\left|\sum_{i=1}^{n}\left(A_\alpha^{\mathcal{C}}p_\alpha\right)_i\right|j\right\rangle\left\langle j\left|\sum_{i=1}^{n}\left(\nabla_\beta\Lambda p_\beta\right)_i\right|a\right\rangle\right)\end{aligned} \tag{23}$$

$$\begin{aligned}&\left(\nabla_\alpha\Lambda p_\alpha, \nabla_\beta\Lambda p_\beta\right)_{-1}\\ &\quad=\frac{1}{\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left(\left\langle a\left|\sum_{i=1}^{n}\left(\nabla_\alpha\Lambda p_\alpha\right)_i\right|j\right\rangle\left\langle j\left|\sum_{i=1}^{n}\left(\nabla_\beta\Lambda p_\beta\right)_i\right|a\right\rangle\right)\end{aligned} \tag{24}$$

have been employed (corresponding conditions for invariance of nuclear magnetic shielding tensor are examined in Ref. [12]).

The same formulae are established using the hypervirial theorem, via the off-diagonal relationship

$$\left\langle j \left| \sum_{i=1}^{n} (\nabla\Lambda \cdot \mathbf{p})_i \right| a \right\rangle = i m_e \omega_{ja} \left\langle j \left| \sum_{i=1}^{n} \Lambda_i \right| a \right\rangle \tag{25}$$

and the operator equations

$$\frac{i m_e}{\hbar} [H^{(0)}, \Lambda] = \nabla\Lambda \cdot \mathbf{p}, \tag{26}$$

$$[\Lambda, [\Lambda, H^{(0)}]] = -\frac{\hbar^2}{m_e} (\nabla\Lambda)^2. \tag{27}$$

These results can be used to work out explicit conditions for invariance of molecular magnetic susceptibilities corresponding to a specific form of Λ [9]. They are analyzed in the next section to check whether a Λ function can be found which would make the functional stationary. The case of nuclear magnetic shielding is comparatively less interesting, as it is immediately seen from eqs. (11) and (12) that the relative functional is characterized by a cross structure which cannot be extremized.

III Variational analysis of the paramagnetic contribution to the interaction energy in a gauge transformation.

The paramagnetic contribution (18) to magnetic susceptibility depends on the excited states, and is much more difficult to estimate than the diamagnetic contribution (16), which is an expectation value over the reference state, usually described with great accuracy via current methods relying on the algebraic approximation. Now, as the sum of diamagnetic and paramagnetic contributions stays the same in the ideal case of exact eigenfunctions to a model hamiltonian, it is obviously advantageous to look for a gauge minimizing the size of the paramagnetic term. In such a case the bulk of the susceptibility would be formally obtained via the expectation value (16), which is expected to be quite good. Therefore, if W_p^{BB} passed through a maximum, the paramagnetic contribution to the susceptibility would reach a minimum, and the requirement for accuracy would be very simply fulfilled. The problem becomes that of maximizing a functional representing the paramagnetic part of the second-order interaction energy W^{BB}, and therefore minimizing the paramagnetic contribution to total average magnetic susceptibility according to eq. (9). Such a functional can be defined as

$$J(\Lambda) = W_p^{\prime BB}(\Lambda) = W_p^{BB}(\mathbf{A}^{\mathcal{C}}) + \Delta_p^{BB}(\Lambda). \tag{28}$$

The λ function corresponding to an extremum of the functional (28) satisfies the first-order necessary condition [16, 17, 18]

$$\frac{\partial}{\partial \varepsilon} J(\lambda + \varepsilon\phi)|_{\varepsilon=0} = \frac{\partial}{\partial \varepsilon} \Delta_p^{BB}(\lambda + \varepsilon\phi)\Big|_{\varepsilon=0} = 0 \tag{29}$$

(where ϵ is a parameter continuously varying in a given interval, and $\phi = \phi(\mathbf{r})$ is a variation function), because W_p^{BB} is independent of Λ. Working expressions for $J(\Lambda)$ are found replacing Λ by $\lambda + \epsilon\phi$ in eqs. (28) and (19). ¿From now on, the following definitions are employed to simplify the notation

$$c_{aj} = \left\langle a \left| \sum_{i=1}^{n} \left(A_\alpha^{\mathcal{C}} p_\alpha \right)_i \right| j \right\rangle \tag{30}$$

$$z_{ja}(\Lambda) = \left\langle j \left| \sum_{i=1}^{n} \left(\nabla_\beta(\Lambda) p_\beta \right)_i \right| a \right\rangle \tag{31}$$

$$z_{aj}(\Lambda) = \left\langle a \left| \sum_{i=1}^{n} \left(\nabla_\alpha(\Lambda) p_\alpha \right)_i \right| j \right\rangle . \tag{32}$$

Accordingly, eq. (19) takes the form

$$\Delta_p^{BB}(\Lambda) = -\frac{e^2}{2m_e^2 c^2 \hbar} \sum_{j \neq a} \frac{2}{\omega_{ja}} \operatorname{Re}\left[2 c_{aj} z_{ja}(\Lambda) + z_{aj}(\Lambda) z_{ja}(\Lambda)\right] \tag{33}$$

or, writing the integrals in full and summing over repeated $\alpha = x, y, z$,

$$\Delta_p^{BB}(\Lambda) = -\frac{e^2}{2m_e^2 c^2 \hbar}$$

$$\times \left\{ 2\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left(c_{aj}\sum_{k=1}^{n}\int \Psi_j^{(0)*}(\mathbf{r})\frac{\partial\Lambda(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_a^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)\right.$$
$$+\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left[\left(\sum_{k=1}^{n}\int \Psi_a^{(0)*}(\mathbf{r})\frac{\partial\Lambda(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_j^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)\right.$$
$$\left.\left.\times\left(\sum_{k=1}^{n}\int \Psi_j^{(0)*}(\mathbf{r})\frac{\partial\Lambda(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_a^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)\right]\right\}, \tag{34}$$

where $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, ...\mathbf{r}_n)$ denotes the set of electron coordinates. By replacing Λ by $\lambda + \varepsilon\phi$ in this equations, one finds

$$\frac{\partial}{\partial\varepsilon}J(\lambda + \varepsilon\phi)|_{\varepsilon=0} = -\frac{e^2}{2m_e^2c^2\hbar}$$
$$\times \left\{ 2\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left(c_{aj}\sum_{k=1}^{n}\int \Psi_j^{(0)*}(\mathbf{r})\frac{\partial\phi(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_a^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)\right.$$
$$+\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left[\left(\sum_{k=1}^{n}\int \Psi_a^{(0)*}(\mathbf{r})\frac{\partial\phi(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_j^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)\right.$$
$$\times\left(\sum_{k=1}^{n}\int \Psi_j^{(0)*}(\mathbf{r})\frac{\partial\lambda(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_a^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)$$
$$+\left(\sum_{k=1}^{n}\int \Psi_a^{(0)*}(\mathbf{r})\frac{\partial\lambda(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_j^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)$$
$$\left.\left.\times\left(\sum_{k=1}^{n}\int \Psi_j^{(0)*}(\mathbf{r})\frac{\partial\phi(\mathbf{r})}{\partial\alpha_k}\frac{\hbar}{i}\frac{\partial\Psi_a^{(0)}(\mathbf{r})}{\partial\alpha_k}d\mathbf{r}_1\ldots d\mathbf{r}_n\right)\right]\right\}$$
$$= -\frac{e^2}{2m_e^2c^2\hbar}\left\{2\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left[c_{aj}z_{ja}(\phi)\right]\right.$$
$$\left.+\sum_{j\neq a}\frac{2}{\omega_{ja}}\,\mathrm{Re}\left[z_{aj}(\phi)z_{ja}(\lambda)+z_{aj}(\lambda)z_{ja}(\phi)\right]\right\} = 0. \tag{35}$$

¿From the relations

$$\left\langle i\left|O^{+}\right|j\right\rangle = (O^{+})_{ij} = \langle j\,|O|\,i\rangle^{*} = (O)_{ji}{}^{*} \tag{36}$$

that hold for any operator O, and considering that $O = \nabla\Lambda \cdot \mathbf{p}$ is a hermitian operator, $O^{+} = O$, it is immediately obtained that

$$z_{aj}(\phi)z_{ja}(\lambda) + z_{aj}(\lambda)z_{ja}(\phi) = 2\,\mathrm{Re}\left[z_{ja}(\phi)z_{aj}(\lambda)\right], \tag{37}$$

and since

$$z_{ja}(\phi) = z_{aj}^{*}(\phi), \tag{38}$$

eq. (35) becomes

$$-\frac{e^2}{2m_e^2 c^2 \hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}} 2\,\mathrm{Re}\left[c_{aj}z_{ja}(\phi) + z_{ja}(\phi)z_{aj}(\lambda)\right] = 0. \tag{39}$$

As this relationship is valid for any ϕ function, then,

$$\mathrm{Re}\left\{\left[c_{aj} + z_{aj}(\lambda)\right] z_{ja}(\phi)\right\} = 0. \tag{40}$$

Defining $z_1 = a + ib = c_{aj} + z_{aj}(\Lambda)$, and $z_2 = c + id = z_{ja}(\phi)$, it is obtained that $ac - bd = 0$: since this relation is valid for infinite values of c and d, the condition $a = b = 0$ must be fulfilled, and we conclude that

$$c_{aj} + z_{aj}(\lambda) = 0, \tag{41}$$

$$\Delta_p^{BB}(\lambda) = \frac{e^2}{2m_e^2 c^2 \hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\left|c_{aj}\right|^2. \tag{42}$$

From

$$W_p^{BB}(\mathbf{A}^{\mathcal{C}}) = -\frac{e^2}{2m_e^2 c^2 \hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\left|c_{aj}\right|^2 \tag{43}$$

it is finally concluded that

$$W_p^{\prime BB}(\mathbf{A}') = W_p^{BB}(\mathbf{A}^{\mathcal{C}}) + \Delta_p^{BB}(\lambda) = 0. \tag{44}$$

This relationship means that the transformed vector potential is exactly zero, which is not possible, since $\mathbf{A}'$ should correspond to the same magnetic field as $\mathbf{A}^{\mathcal{C}}$. Therefore, an extremum has only been reached by *reductio ad adsurdum*. Accordingly, it is not possible to find a λ function which minimizes the paramagnetic part of the susceptibility in a variational sense, that is yielding an absolute minimum.

The same contradiction is found if the $\Delta_p^{BB}(\Lambda)$ expression valid for *exact* solutions of the Schrödinger equation, compare for eqs. (17) and (20), is employed. In this case

$$\Delta_p^{BB}(\Lambda) = -\frac{e^2}{2m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \left[2\mathbf{A}^C \cdot \nabla\Lambda + (\nabla\Lambda)^2 \right]_i \right| a \right\rangle . \tag{45}$$

Accordingly, owing to eq. (20), and to the fact that the sum of $W_d^{BB} + W_p^{BB}$ in eq. (9) is invariant to a gauge transformation for exact eigenfunctions, one could alternatively try to maximize functional (28) via a procedure which actually amounts to minimizing the diamagnetic contribution $W_d^{BB} = -(1/2)\chi^{\mathrm{d}}_{\alpha\beta} B_\alpha B_\beta$ to the energy functional, see also eqs. (14), (16), and (17). Therefore, replacing again Λ by $\lambda + \varepsilon\phi$, and performing the differentiation,

$$\left. \frac{\partial}{\partial\varepsilon} J(\lambda + \varepsilon\phi) \right|_{\varepsilon=0} = -\frac{e^2}{2m_e c^2} \left\langle a \left| \sum_{i=1}^{n} \left[2(\mathbf{A}^C + \nabla\lambda) \cdot \nabla\phi \right]_i \right| a \right\rangle = 0, \tag{46}$$

i.e., $\nabla\lambda = -\mathbf{A}^{\mathcal{C}}$, for any increment function ϕ, and the conclusion would be again that the transformed vector potential $\mathbf{A}' = \mathbf{A}^{\mathcal{C}} + \nabla\lambda$ vanishes identically all over the molecular domain, which is clearly meaningless. Therefore one is left only with the possibility of finding *local* extremum points for a given type of Λ function. In principle they can be determined by expressing Λ via some general polynomial form. These local extremum points would depend on the type of molecule, on its geometry, and on the basis set employed in the calculation of magnetic properties. Their theoretical interest is clearly limited, however an analysis is provided in the next Section.

IV Local maxima of the diamagnetic contribution to susceptibility

In deriving the results of Sec. III we used the fact that, in general, for λ such that the first differential $d\Delta_p^{BB}(\lambda) = 0$, and the second differential $d^2\Delta_p^{BB}(\lambda)$ is a negative definite quadratic form, the functional $\Delta_p^{BB}(\lambda)$ is an absolute maximum, corresponding to a minimum of the paramagnetic contribution to molecular susceptibility. Let us denote the second differential by the bilinear form

$$d^2 f(\mu)(\varphi, \psi) = \frac{\partial}{\partial\epsilon} df(\mu + \epsilon\varphi)(\psi)|_{\epsilon=0}. \tag{47}$$

Then, choosing $\mu = \lambda$ and $\varphi = \psi = \Lambda - \lambda$, from the necessary condition (29), assuming that identity (20) is satisfied (which is only true in the ideal case of exact eigenfunctions to a model hamiltonian), and from

$$\Delta_p^{BB}(\Lambda) = -\left\langle 0|2\mathbf{A}^{\mathcal{C}} \cdot \nabla\Lambda + |\nabla\Lambda|^2|0\right\rangle, \tag{48}$$

$$\Delta_p^{BB}(\lambda) = -\left\langle 0|2\mathbf{A}^{\mathcal{C}} \cdot \nabla\lambda + |\nabla\lambda|^2|0\right\rangle, \tag{49}$$

$$\frac{1}{2}d^2\Delta_p^{BB}(\lambda)(\Lambda - \lambda, \Lambda - \lambda) = -\left\langle 0\left|\frac{1}{2}\left[\nabla(\Lambda - \lambda)\right]^2\right|0\right\rangle, \tag{50}$$

and $\mathbf{A}^{\mathcal{C}} = -\nabla\lambda$, because λ is a critical point, we obtain for any Λ:

$$\begin{aligned} &\Delta_p^{BB}(\Lambda) - \Delta_p^{BB}(\lambda) - \frac{1}{2}d^2\Delta_p^{BB}(\lambda)(\Lambda - \lambda, \Lambda - \lambda) \\ &= -\left\langle 0\left|2\mathbf{A}^{\mathcal{C}} \cdot \nabla(\Lambda - \lambda) + |\nabla\Lambda|^2 - |\nabla\lambda|^2 - \frac{1}{2}\left[\nabla(\Lambda - \lambda)\right]^2\right|0\right\rangle \\ &= -\frac{1}{2}\left\langle 0\right|\left[\,\nabla(\Lambda - \lambda)\right]^2|0> \leq 0 \end{aligned} \tag{51}$$

Hence,

$$\Delta_p^{BB}(\Lambda) \leq \Delta_p^{BB}(\lambda) + \frac{1}{2}d^2\Delta_p^{BB}(\lambda)(\Lambda - \lambda, \Lambda - \lambda) < \Delta_p^{BB}(\lambda) \tag{52}$$

and the proof is complete.

Lets us now study some special Λ sets suitable to maximize the diamagnetic contribution W_d^{BB}, see discussion preceding eq. (46). Polynomial forms of the Λ function are proposed and analyzed hereafter:

i) For $\Lambda(x,y,z) = ax^2 + by^2 + cz^2$, denoting by $|0\rangle$ the wave function of the ground state, from the necessary condition (29), assuming that identity (20) is satisfied, one obtains the coefficients:

$$\begin{aligned} a &= \frac{\langle 0|xy|0\rangle\, B_3 - \langle 0|xz|0\rangle\, B_2}{4\,\langle 0|xx|0\rangle} \\ b &= \frac{\langle 0|yz|0\rangle\, B_1 - \langle 0|xy|0\rangle\, B_3}{4\,\langle 0|yy|0\rangle} \\ c &= \frac{\langle 0|xz|0\rangle\, B_2 - \langle 0|yz|0\rangle\, B_1}{4\,\langle 0|zz|0\rangle} \end{aligned} \tag{53}$$

with $\mathbf{B} = (B_1, B_2, B_3)$ the x, y and z cartesian components of the magnetic field. We remark that $\langle 0|xx|0\rangle$, $\langle 0|yy|0\rangle$, and $\langle 0|zz|0\rangle$ are not zero, because the integral of a positive function is zero only on zero measure subsets of R^n, and, in this case, the subset of integration is R^n, that has positive measure.

For the HF, H_2O, NH_3, CH_4 molecules, assuming the principal axis system retained in the calculations of Ref. [10], $\Lambda \equiv 0$, and we conclude that it is not possible to find a gauge transformation maximizing the diamagnetic contribution to magnetic susceptibility for this set of molecules via the polynomial expression $\Lambda(x, y, z) = ax^2 + by^2 + cz^2$.

ii) Let us now consider another polynomial form, $\Lambda(x, y, z) = ax^2 + by^2 + cz^2 + dxy + eyz + fzx$, and the numerical values for the average second moment, obtained for hydrogen fluoride, ammonia and methane via basis set IV of Ref. [10], and via basis set VI of Ref. [11] for water. For the HF molecule, with the z axis oriented in the direction of the bond, one obtains the following parameters: $a = 0$, $b = 0$, $c = 0$, $d = 0$, $e = 0.05483B_1$, $f = -0.05483B_2$, and

$$\lambda(x, y, z) = 0.05483(B_1 y - B_2 x)z. \tag{54}$$

For the H_2O molecule one finds $a = 0$, $b = 0$, $c = 0$, $d = 0.0636142B_3$, $e = -0.025335B_1$, $f = -0.0385275B_2$, and

$$\lambda(x, y, z) = 0.0636142B_3 xy - (0.025335B_1 y + 0.0385275B_2 x)z. \tag{55}$$

For the NH_3 molecule $a = 0$, $b = 0$, $c = 0$, $d = 0$, $e = -0.395907B_1$, $f = 0.395907B_2$, and

$$\lambda(x, y, z) = -0.395907(B_1 y - B_2 x)z. \tag{56}$$

Eventually, for the CH_4 molecule, one obtains $a = 0$, $b = 0$, $c = 0$, $d = 0$, $e = 0$, $f = 0$ by symmetry, then $\lambda \equiv 0$, and we conclude that it is not possible to find a gauge transformation maximizing $J(\Lambda)$ for this molecule using a polynomial expression of type (ii).

The functions $\lambda(a, b, c)$ with a, b, c, given in eqs. (53)-(56) correspond to a local maximum of the functional Δ_p^{BB}, because the second derivative of Δ_p^{BB} evaluated via $\lambda(abc)$ is negative.

V Conclusions

A general form of λ function satisfying the extremum condition (35), corresponding to a minimum (maximum) of the paramagnetic (diamagnetic) contribution to magnetic susceptibility cannot be found. Instead, one can find particular λ transformations yielding a local minimum of the paramagnetic susceptibility for a given molecule.

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