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Magnetic screening of nuclei by electrons as manifestation of geometric vector potential

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Summary. The usual Born–Oppenheimer approach to a molecule in a magnetic field leads to an effective nuclear hamiltonian in which bare nuclei interact with the field. We show that the geometric phase, which has been the object of much interest in recent years, is capable of correcting this defect, accounting for corrections to the molecular charge and magnetic moment due to the electron cloud accompanying the nuclei.

Key words: Molecules – Phase factors – Magnetic interactions

1. Introduction

The geometric phase, some of whose effects have been known for some time in molecular systems, has recently received wide attention as a universal phenomenon, manifesting itself in many areas of physical science [1, 2]. In the molecular context, the geometric phase is just the change of phase which a Born–Oppenheimer electronic wave function may experience when it is smoothly carried around a closed path in nuclear configuration space subject to certain conditions.

The case which has been the subject of the most study is that of a Born–Oppenheimer electronic function, required to be real, and continuously and smoothly evolving while the nuclei are transported around a closed path. Since the electronic function is real, the only phase change it can experience is a sign change, and this sign change occurs when the path encloses a conical intersection of two electronic potential energy surfaces [3, 4]. The resulting double-valuedness of the electronic part of the molecular wave function can be compensated by a rephasing (meaning that the wave function is no longer real but is single-valued), but at the cost of introducing a vector potential term (geometric vector potential) into the effective Schrödinger equation for the nuclear motion [5]. This has consequences for the energy levels of certain molecules, of which the metal trimers have been most extensively studied [6, 7]. Since the appearance of the paper by Berry [8], there has been a great deal of interest in applications of the phase to various physical situations.

For nondegenerate electronic levels, it is a consequence of time reversal invariance that there can be no geometric phase change unless the path encloses an intersection, and then only the above-mentioned sign change [5]. If an external magnetic field is applied, however, the time reversal invariance is broken, and there will be a geometric phase, not necessarily a sign change; or, if single-valuedness is required of the electronic wave function, there will be a geometric vector potential in the nuclear Schrödinger equation. The geometric vector potential will be added to the vector potential of the external field, bringing about a modification of the effect of the field on the nuclear motion. Moreover, the geometric vector potential, which would be zero in the absence of the external field, is clearly a function of the external field, linear in lowest approximation, and can be thought of as induced by the external field. One expects, therefore, that it represents some aspect of the magnetic shielding of the nuclei by the electrons. In this paper, we analyze some simple aspects of this effect.

The Born–Oppenheimer treatment of molecular systems in external magnetic fields has been considered in some detail by Schmelcher, Cederbaum, and Meyer [9, 10]. They showed that the conventional treatment leads to equations of motion in which the external field acts on bare nuclei which are completely unshielded by the electrons. By rephasing the electronic wave function so that, at least at infinite separation, one achieves a consistent gauge, they obtained what they called the "screened Born–Oppenheimer approximation," in which this defect is removed. As we shall see, this screening of the nuclei by the electrons can also (and equivalently) be understood as a manifestation of the geometric vector potential. Indeed, it has already been noticed by Cottingham and Hassan [11] that an external magnetic field induces a geometric vector potential; they carried out an approximate calculation for the H_2^+ ion, obtaining about a 5% reduction in the effective field.

In this paper, we take up the general theory of the geometric vector potential induced by an external magnetic field, and verify that it just reproduces some of the effects that, intuitively, one would expect to be present. We first obtain a few general relations, and then apply them to the translational and rotational motion of molecules. In both cases, the results correspond to intuition: The action of the external field on the translational motion of a molecule is determined by the total charge of the molecule, not just that of the nuclei. For the rotation of the diatomic, the effect is to replace the magnetic moment due to bare nuclei by the total magnetic moment of the molecule, including the electrons. In both cases, we limit our considerations to terms of first order in the external field. In the treatment of the translational motion, we do not require the field to be uniform, but we do make this assumption in our treatment of the rotation of the diatomic, as well as the assumption that nuclear centers of mass and charge coincide. For vibrational degrees of freedom, the situation is more complicated, as one would expect, and we confine ourselves to a few qualitative remarks.

2. General relations

The state of a molecular system can evidently always be represented as a ket $|\Psi(\boldsymbol{R})\rangle$ in the Hilbert space of the electronic degrees of freedom which is a function of the nuclear coordinates, collectively denoted by $\boldsymbol{R}$. In the Born–Oppenheimer treatment, we approximate $|\Psi(\boldsymbol{R})\rangle$ by the product:

$$|\Psi(\boldsymbol{R})\rangle \cong |\chi(\boldsymbol{R})\rangle\psi(\boldsymbol{R}), \tag{1}$$

where $\psi(\boldsymbol{R})$ is a wave function representing the nuclear motion and $|\chi(\boldsymbol{R})\rangle$ is the electronic eigenket, which is normalized and satisfies:

$$\{\hat{H}(\boldsymbol{R}) - U(\boldsymbol{R})\}|\chi(\boldsymbol{R})\rangle = 0, \tag{2}$$

where $\hat{H}(\boldsymbol{R})$ is the $\boldsymbol{R}$-dependent electronic hamiltonian, comprising everything in the total molecular hamiltonian except the nuclear kinetic energy, and $U(\boldsymbol{R})$ is its eigenvalue.

Now consider the contribution of the nuclear degree of freedom x_μ to the kinetic energy, as applied to the approximate state function of Eq. (1). The well-known result [5] is:

$$\frac{1}{2M}\hat{p}_\mu^2|\Psi\rangle = -\frac{\hbar^2}{2M}\partial_\mu\partial_\mu|\Psi\rangle \cong -\frac{\hbar^2}{2M}\{|\chi\rangle\partial_\mu^2\psi + 2|\partial_\mu\chi\rangle\partial_\mu\psi + |\partial_\mu^2\chi\rangle\psi\}, \tag{3}$$

where ∂_μ stands for $\partial/\partial x_\mu$. We obtain an approximate expression for the nuclear kinetic energy operator operating on ψ alone by taking the inner product of Eq. (3) with the bra $\langle\chi|$. The result can be represented as follows:

$$\left\langle\chi\left|\frac{1}{2M}\hat{p}_\mu^2\Psi\right.\right\rangle = \frac{1}{2M}\{(\hat{p}_\mu + \hbar f_\mu)^2\psi + \hbar^2 G_\mu\psi\}, \tag{4}$$

where

$$f_\mu = \left\langle\chi\left|\frac{1}{i}\partial_\mu\chi\right.\right\rangle \tag{5}$$

and

$$G_\mu = -\langle\chi|\partial_\mu^2\chi\rangle - \frac{1}{i}\partial_\mu f_\mu - f_\mu^2. \tag{6}$$

The term involving G_μ can be absorbed into the potential energy, and is thus relatively uninteresting; f_μ, however, acts as a vector potential-like term, leading to qualitatively different effects [5]. It is called the geometric vector potential. For electronic states which are nondegenerate for all $\boldsymbol{R}$, in the absence of an external magnetic field, it is a consequence of time-reversal invariance (or equivalently, of the possibility of choosing the electronic wave function to be real) that $f_\mu = 0$. Here, however, we are interested in the case of a molecular system in the presence of an external magnetic field, for which in general $f_\mu \neq 0$.

Since the molecular state function $|\Psi(\boldsymbol{R})\rangle$ must clearly be single-valued, one obtains an effective nuclear Schrödinger equation with single-valued boundary conditions only if the electronic part $|\chi\rangle$ is also single-valued as a function of $\boldsymbol{R}$. If we have at our disposal a single-valued $|\chi\rangle$, f_μ can be evaluated directly from Eq. (5). In some cases, however, this is not convenient, so it is useful to study some properties of the geometric vector potential. To do this, we define an operator $\hat{g}_\nu$ by the relation:

$$\partial_\nu|\chi\rangle = i\hat{g}_\nu|\chi\rangle. \tag{7}$$

$\hat{g}_\mu$ is thus an operator in the *electronic* Hilbert space which reproduces the infinitesimal change in the eigenfunction when the nuclear coordinates are altered by an infinitesimal amount. Taking a second partial derivative with respect to another degree of freedom, we obtain:

$$\partial_\mu\partial_\nu|\chi\rangle = i(\partial_\mu\hat{g}_\nu)|\chi\rangle - \hat{g}_\nu\hat{g}_\mu|\chi\rangle. \tag{8}$$

Taking the second partial derivative also in the reverse order, and requiring single-valuedness of $|\chi\rangle$, we find:

$$(\partial_\mu \partial_\nu - \partial_\nu \partial_\mu)|\chi\rangle = 0 = \{i(\partial_\mu \hat{g}_\nu - \partial_\nu \hat{g}_\mu) + [\hat{g}_\mu, \hat{g}_\nu]\}|\chi\rangle = 0. \tag{9}$$

We now take the diagonal element of Eq. (9), noting that, for instance, because of Eqs. (5) and (7):

$$\langle\chi|\partial_\mu \hat{g}_\nu|\chi\rangle = \partial_\nu f_\nu + i\langle\chi|[\hat{g}_\mu, \hat{g}_\nu]|\chi\rangle. \tag{10}$$

Combining Eq. (10) with Eq. (9), we finally obtain:

$$\partial_\mu f_\nu - \partial_\nu f_\mu = \frac{1}{i}\langle\chi|[\hat{g}_\mu, \hat{g}_\nu]|\chi\rangle. \tag{11}$$

Equation (11) closely resembles the expression for a magnetic field strength as the curl of a vector potential, and the right-hand side is frequently called the field strength.

To determine the operators $\hat{g}_\mu$, we differentiate Eq. (2), using Eq. (7) to obtain:

$$\partial_\mu\{(\hat{H} - U)|\chi\rangle\} = 0 = (\partial_\mu \hat{H} - \partial_\mu U)|\chi\rangle + i(\hat{H} - U)\hat{g}_\mu|\chi\rangle, \tag{12}$$

or

$$i[\hat{g}_\mu, \hat{H}]|\chi\rangle = (\partial_\mu \hat{H} - \partial_\mu U)|\chi\rangle. \tag{13}$$

Both sides of Eq. (13) are entirely off-diagonal, so the diagonal part of $\hat{g}_\mu$ is left undetermined by Eq. (13). Making the off-diagonal nature explicit, and also making use of the relation between commutator and time derivative, we can write an operator equation equivalent to Eq. (13):

$$i[\hat{g}_\mu, \hat{H}] = -\hbar\hat{\dot{g}}_\mu = (\partial_\mu \hat{H})_{\mathrm{od}}, \tag{14}$$

where the subscript od stands for off-diagonal.

The geometric vector potential f_μ is a diagonal matrix element of $\hat{g}_\mu$, according to Eqs. (5) and (7). However, only the off-diagonal part is determined by Eq. (13) or (14); the diagonal part f_μ must be determined by the single-valuedness condition of Eq. (11). Since any diagonal element of $\hat{g}_\mu$ will in any case contribute nothing to the commutator in Eq. (11), for the purpose of calculating that commutator we can let $\hat{g}_\mu$ have any diagonal part we wish. We can thus drop the subscript od and simply write:

$$i[\hat{g}_\mu, \hat{H}] = -\hbar\hat{\dot{g}}_\mu = (\partial_\mu \hat{H}), \tag{15}$$

with the understanding that the $\hat{g}_\mu$ thus obtained will not be used to calculate f_μ directly via Eqs. (5) and (7), but only to insert into the commutator on the right side of Eq. (11), from which f_μ will then be determined.

3. Translational motion of molecule

In this section, we are concerned only with rigid translation of a molecular system in an external magnetic field; the field need *not* be assumed uniform. We will calculate the effect of the geometric vector potential through the first order in the external field.

In order to concentrate on translational motion only, we treat the molecule as rigid, and not allowed to rotate. Its total momentum is:

$$\hat{\boldsymbol{P}} = \sum_j \hat{\boldsymbol{p}}_j, \tag{16}$$

where the sum goes over all the nuclei. The corresponding kinetic energy is:

$$\hat{T} = \frac{1}{2M}(\hat{\boldsymbol{P}} + \boldsymbol{F})^2, \tag{17}$$

where

$$\boldsymbol{F} = -\frac{e}{c}\sum_j Z_j \boldsymbol{A}(\boldsymbol{r}_j), \tag{18}$$

e is the electronic charge (taken as a positive quantity), c is the speed of light, Z_j is the atomic number of nucleus j, and $\boldsymbol{A}$, of course, is the vector potential. The effect of $\boldsymbol{F}$ on the motion is determined only by its curl, given by:

$$\nabla \times \boldsymbol{F} = -\frac{e}{c}\sum_j Z_j \boldsymbol{B}(\boldsymbol{r}_j), \tag{19}$$

where $\boldsymbol{B}$ is the external field. This corresponds to an effective magnetic field equal to the weighted average of the fields at the locations of all the nuclei.

According to Eq. (4), there may be an additional term $\hbar \boldsymbol{f}$ in addition to $\boldsymbol{F}$, which is to be determined by the methods developed in the last section. For the gradient of the electronic hamiltonian with respect to the translational coordinate, we have in vector notation:

$$\nabla \hat{H} = \sum_j \nabla_j \hat{H} = \boldsymbol{F}_{\mathrm{en}}, \tag{20}$$

where $\boldsymbol{F}_{\mathrm{en}}$ stands for the total electrostatic force exerted on the electrons by the nuclei. It is also the *total* force exerted on all the electrons minus the magnetic force, since the total electrostatic force exerted on the electrons by each other sums to zero. We thus have, using Eq. (15):

$$-\hbar \dot{\hat{\boldsymbol{g}}} = \sum_\alpha \frac{d}{dt}\left\{\hat{\boldsymbol{p}}_\alpha + \frac{e}{c}\boldsymbol{A}(\boldsymbol{r}_\alpha)\right\} + \frac{e}{c}\sum_\alpha \dot{\hat{\boldsymbol{r}}}_\alpha \times \boldsymbol{B}(\boldsymbol{r}_\alpha), \tag{21}$$

where the sum now goes over the electrons. Formally integrating Eq. (21), we find:

$$\hat{\boldsymbol{g}} = -\frac{1}{\hbar}\sum_\alpha m\dot{\hat{\boldsymbol{r}}}_\alpha + \frac{e}{\hbar c}\sum_\alpha \hat{\boldsymbol{q}}_\alpha = -\frac{1}{\hbar}\sum_\alpha \left\{\hat{\boldsymbol{p}}_\alpha + \frac{e}{c}\boldsymbol{A}(\boldsymbol{r}_\alpha)\right\} + \frac{e}{\hbar c}\sum_\alpha \hat{\boldsymbol{q}}_\alpha, \tag{22}$$

where $\hat{\boldsymbol{q}}_\alpha$ is determined by:

$$\dot{\hat{\boldsymbol{q}}}_\alpha = \boldsymbol{B}(\boldsymbol{r}_\alpha) \times \dot{\hat{\boldsymbol{r}}}_\alpha. \tag{23}$$

We note that, for a uniform field with $\boldsymbol{A} = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r}$, we would have exactly:

$$\hat{\boldsymbol{q}}_\alpha = 2\boldsymbol{A}(\boldsymbol{r}_\alpha). \tag{24}$$

We now proceed to calculate the commutator of two components of $\hat{\boldsymbol{g}}$, through the first order in the external field. Taking the x and y components as typical examples, we obtain from Eq. (22):

$$[\hat{g}_x, \hat{g}_y] = \sum_\alpha \left\{\frac{1}{\hbar^2}\left[\left(\hat{p}_{\alpha x} + \frac{e}{c}A_x(\boldsymbol{r}_\alpha)\right), \left(\hat{p}_{\alpha y} + \frac{e}{c}A_y(\boldsymbol{r}_\alpha)\right)\right] - \frac{em}{\hbar^2 c}([\dot{\hat{x}}_\alpha, \hat{q}_{\alpha y}] + [\hat{q}_{\alpha x}, \dot{\hat{y}}_\alpha])\right\} \tag{25}$$

where we have omitted commutators of $\hat{q}_{\alpha x}$, $\hat{q}_{\alpha y}$ because this contribution would be second order in the external field.

The first commutator on the right side of Eq. (25) just gives $(e/i\hbar c)\boldsymbol{B}(\boldsymbol{r}_\alpha)$. The others are harder because we do not have an explicit expression for $\hat{\boldsymbol{q}}_\alpha$, only for its time derivative. To obtain these commutators, we make use of the relation:

$$[\hat{\dot{x}}, \hat{q}_y] = \frac{d}{dt}[\hat{x}, \hat{q}_y] + [\hat{\dot{q}}_y, \hat{x}]. \tag{26}$$

We are only interested in a diagonal element of this commutator, and the total time derivative on the right side of Eq. (26) clearly contributes nothing to this. For calculating diagonal elements, therefore, we can make the replacement:

$$[\hat{\dot{x}}, \hat{q}_y] = [\hat{\dot{q}}_y, \hat{x}] = \left[\left\{\frac{B_z}{m}\left(\hat{p}_x + \frac{e}{c}A_x\right) - \frac{B_x}{m}\left(\hat{p}_z + \frac{e}{c}A_z\right)\right\}, \hat{x}\right] = \frac{\hbar B_z}{im}. \tag{27}$$

Evaluating the other commutator in the same way and plugging into Eq. (25), we find:

$$\langle\chi|[\hat{g}_x, \hat{g}_y]|\chi\rangle = -\frac{e}{i\hbar c}\sum_\alpha \langle\chi|B_z(\boldsymbol{r}_\alpha)|\chi\rangle. \tag{28}$$

Putting this into Eq. (11) and comparing with Eq. (4), we find

$$\hbar\nabla \times \boldsymbol{f} = \frac{e}{c}\sum_\alpha \langle\chi|\boldsymbol{B}(\boldsymbol{r}_\alpha)|\chi\rangle. \tag{29}$$

The geometric vector potential thus leads to an additional force just equal to the total magnetic force on the electronic charge distribution. In particular, if the field is uniform and the molecule neutral, there will be total cancellation. This is, of course, more or less what one would expect intuitively; but one must include the geometric phase in order to obtain it in a Born–Oppenheimer treatment.

4. Rotation of diatomic molecule

In this section, we consider a diatomic molecule, treated as a rigid rotor, in an external magnetic field $\boldsymbol{B}$ which is now assumed to be uniform, so that the vector potential can be taken as $\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r}$. Furthermore, to avoid nonessential complications, we confine our attention to diatomics in $^1\Sigma$ states, and for which the centers of nuclear mass and charge coincide: Designating mass and atomic number of nucleus 1 respectively as M_1, Z_1, with corresponding notation for nucleus 2, we thus require:

$$Z_1 M_2 = Z_2 M_1. \tag{30}$$

A special case of Eq. (30), of course, is that of a homonuclear diatomic molecule. Defining center-of-mass coordinate and momentum vectors $\boldsymbol{R}$, $\boldsymbol{P}$, and with $\boldsymbol{r}$, $\boldsymbol{p}$ for relative coordinate and momentum, and making use of Eq. (30), we find for the nuclear kinetic energy:

$$\hat{T} = \frac{1}{2M}\left\{\hat{\boldsymbol{P}} - \frac{Ze}{2c}(\boldsymbol{B} \times \boldsymbol{R})\right\}^2 + \frac{1}{2\mu}\left\{\hat{\boldsymbol{p}} - \frac{Ze\mu}{2Mc}(\boldsymbol{B} \times \boldsymbol{r})\right\}^2, \tag{31}$$

where Z is total charge, M is total mass, and μ is the reduced mass for the system of two nuclei. The effect of the external field on the center-of-mass contribution can be treated by the methods of the preceding section. Here we concentrate on the relative motion, for which the hamiltonian, to lowest order in the external field, is:

$$\hat{H}_{\text{rel}} = \frac{1}{2\mu}\hat{p}^2 - \frac{Ze\hbar}{2Mc}\boldsymbol{B}\cdot\hat{\boldsymbol{L}}, \tag{32}$$

where $\hat{\boldsymbol{L}}$ is the nuclear angular momentum in units of $\hbar$. We also treat the molecule as rigidly rotating, suppressing the stretching vibration, so that the first term in Eq. (32) is replaced by:

$$\frac{1}{2\mu}\hat{p}^2 = \frac{\hbar^2}{2\mu r^2}\hat{L}^2, \tag{33}$$

where r is now the fixed distance between the two nuclei.

We take the z-direction to be that of $\boldsymbol{B}$, with the x- and y-directions orthogonal to z and to each other, but otherwise arbitrary; and we define molecule-fixed coordinates ζ, ξ, η, with the ζ-direction along the internuclear axis, making an angle θ with $\boldsymbol{B}$; the ξ-direction in the $z\zeta$ plane, making an angle $(\theta + (\pi/2))$ with $\boldsymbol{B}$; and the η-direction determined by ζ and ξ by the right-hand rule. In terms of the angle θ and a longitude angle ϕ giving the angle between the $\zeta\xi$ and zx planes, we have explicitly:

$$\begin{aligned}\zeta &= z\cos\theta + x\sin\theta\cos\phi + y\sin\theta\sin\phi;\\ \xi &= -z\sin\theta + x\cos\theta\cos\phi + y\cos\theta\sin\phi;\\ \eta &= -x\sin\phi + y\cos\phi,\end{aligned} \tag{34}$$

with the inverse transformation:

$$\begin{aligned}z &= \zeta\cos\theta - \xi\sin\theta;\\ x &= \zeta\sin\theta\cos\phi + \xi\cos\theta\cos\phi - \eta\sin\phi;\\ y &= \zeta\sin\theta\sin\phi + \xi\cos\theta\sin\phi + \eta\cos\phi.\end{aligned} \tag{35}$$

In terms of the molecule-fixed axes, since there is no nuclear angular momentum in the ζ-direction, we can make the replacement:

$$\hat{L}^2 = \hat{L}_\xi^2 + \hat{L}_\eta^2 \tag{36}$$

in Eq. (33). Since angular momentum, like linear momentum, is a differential operator, when it is applied to a product state of the form of Eq. (1), the effective operator applied to the nuclear function ψ is:

$$\hat{L}_{\text{eff}}^2 = (\hat{L}_\xi + f_\xi)^2 + (\hat{L}_\eta + f_\eta)^2 + G, \tag{37}$$

where

$$\begin{gathered}f_\xi = \langle\chi|\hat{L}_\xi|\chi\rangle; \qquad f_\eta = \langle\chi|\hat{L}_\eta|\chi\rangle;\\ G = \langle\chi|\hat{L}^2|\chi\rangle - f_\xi^2 - f_\eta^2 - (\hat{L}_\xi f_\xi) - (\hat{L}_\eta f_\eta).\end{gathered} \tag{38}$$

To first order in the external field, the electronic hamiltonian is given by:

$$\hat{H} = \hat{H}_0 + \delta\hat{H}, \tag{39}$$

where $\hat{H}_0$ is the hamiltonian in the absence of the field and:

$$\delta\hat{H} = \frac{e\hbar}{2mc}\boldsymbol{B}\cdot\hat{\Lambda} = \frac{e\hbar B}{2mc}(\hat{\Lambda}_\zeta\cos\theta - \hat{\Lambda}_\xi\sin\theta). \tag{40}$$

In Eq. (40), m is the electronic mass and $\hat{\Lambda}$ is total electronic angular momentum in units of $\hbar$.

Denoting the electronic eigenstate in the absence of the field by $|\chi_0\rangle$, and defining an operator $\hat{\kappa}$ by:

$$|\chi\rangle = (1 + i\hat{\kappa})|\chi_0\rangle, \tag{41}$$

we obtain the eigenvalue equation:

$$(\hat{H}_0 + \delta\hat{H})(1 + i\hat{\kappa})|\chi_0\rangle = (U_0 + \delta U)(1 + i\hat{\kappa})|\chi_0\rangle, \tag{42}$$

which in first order reduces to:

$$i[\hat{\kappa}, \hat{H}_0]|\chi_0\rangle = (\delta\hat{H} - \delta U)|\chi_0\rangle. \tag{43}$$

There are two ways in which Eq. (43) simplifies: First, since in a $^1\Sigma$ state all average values of electronic angular momentum are zero, there is no first-order energy correction due to the field, so $\delta U = 0$; second, again because $|\chi_0\rangle$ is a $^1\Sigma$ state, the term in $\hat{\Lambda}_\zeta$ in Eq. (40) just gives zero when inserted into Eq. (43), and may therefore be omitted. We can thus determine $\hat{\kappa}$ for our purposes from the relation:

$$i[\hat{\kappa}, \hat{H}_0] = -\hbar\dot{\hat{\kappa}} = -\frac{e\hbar B \sin\theta}{2mc}\hat{\Lambda}_\xi. \tag{44}$$

Any matrix element of $\hat{\kappa}$ can, of course, be determined from Eq. (44). We are interested in evaluating $\hat{\kappa}$ only to first order in the external field, so we are entitled to use the zero-order form of $\hat{\Lambda}_\xi$:

$$\hat{\Lambda}_\xi = \frac{m}{\hbar}\sum_\alpha (\eta_\alpha\dot{\zeta}_\alpha - \zeta_\alpha\dot{\eta}_\alpha). \tag{45}$$

Integrating Eq. (45), we obtain a formal expression for $\hat{\kappa}$:

$$\hat{\kappa} = \frac{eB \sin\theta}{2\hbar c}\sum_\alpha \int (\eta_\alpha\, d\zeta_\alpha - \zeta_\alpha\, d\eta_\alpha). \tag{46}$$

Since the dependence of $\hat{\kappa}$ on the nuclear coordinates is well-defined and single-valued, it leads to a single-valued electronic wave function, so we are permitted to use the direct method for calculating f_ξ and f_η. We now proceed to do this to first order in the field, using Eqs. (38), (41), and (46). First, from Eqs. (38) and (41), we find:

$$\begin{aligned} f_\xi &= \langle\chi|\hat{L}_\xi|\chi\rangle = -\langle\chi|\hat{\Lambda}_\xi|\chi\rangle \\ &= -\langle\chi_0|(1 - i\hat{\kappa})\hat{\Lambda}_\xi(1 + i\hat{\kappa})|\chi_0\rangle = -i\langle\chi_0|[\hat{\Lambda}_\xi, \hat{\kappa}]|\chi_0\rangle, \end{aligned} \tag{47}$$

where we have of course omitted terms of higher than the first order, and have also made use of the fact that, since $|\chi\rangle$ depends only on coordinates of electrons relative to those of nuclei, a differential operator with respect to nuclear coordinates affects $|\chi\rangle$ in the same way as minus the corresponding electronic differential operator.

Using Eq. (46), we can evaluate the commutator in Eq. (47):

$$\begin{aligned} [\hat{\Lambda}_\xi, \hat{\kappa}] &= \frac{eB \sin\theta}{2i\hbar c}\sum_\alpha \left(\eta_\alpha\frac{\partial}{\partial\zeta_\alpha} - \zeta_\alpha\frac{\partial}{\partial\eta_\alpha}\right)\int (\eta_\alpha\, d\zeta_\alpha - \zeta_\alpha\, d\eta_\alpha) \\ &= \frac{eB \sin\theta}{2i\hbar c}\sum_\alpha (\zeta_\alpha^2 + \eta_\alpha^2). \end{aligned} \tag{48}$$

Taking the diagonal element of Eq. (48) and inserting into Eq. (47), we find:

$$f_\xi = -\frac{eB\sin\theta}{2\hbar c}\sum_\alpha \langle \zeta_\alpha^2 + \tfrac{1}{2}\varrho_\alpha^2\rangle$$

$$\equiv -\frac{eB\sin\theta}{2\hbar c}\langle \zeta^2 + \tfrac{1}{2}\varrho^2\rangle, \tag{49}$$

where $\langle\rangle$ denotes an average with respect to $|\chi_0\rangle$ and $\varrho^2 = \xi^2 + \eta^2$. Of course, in a $^1\Sigma$ state the average of η^2 is just half that of ϱ^2.

Proceeding in a similar way, we find for f_η:

$$f_\eta = \frac{eB\sin\theta}{2\hbar c}\sum_\alpha \langle \xi_\alpha \eta_\alpha\rangle = 0. \tag{50}$$

Inserting Eq. (49) into Eqs. (33) and (37), we find the following first-order geometric correction to the effective nuclear hamiltonian:

$$\hat{H}^{\mathrm{nuc}}_{\mathrm{geom}} = -\frac{e\hbar B\sin\theta}{2\mu c}\frac{\langle \zeta^2 + \frac{1}{2}\varrho^2\rangle}{r^2}\hat{L}_\xi = \frac{e\hbar}{2\mu c}\frac{\langle \zeta^2 + \frac{1}{2}\varrho^2\rangle}{r^2}\boldsymbol{B}\cdot\hat{\boldsymbol{L}}. \tag{51}$$

It is straightforward to verify that the other terms in Eqs. (37), (38) contribute nothing in first order.

Equation (51) is the main result of this section. It accounts for the correction to the magnetic moment of the molecule due to the electrons being carried along with the nuclei.

To obtain a better feeling for the meaning of Eq. (51), we consider the limiting case in which the nuclear separation r is very large, and the molecule is split into two neutral atoms. We note also that rotations of the nuclei are with nuclear center of mass held fixed, i.e., they are taken about the center of mass; the coordinate ζ must therefore be measured relative to the center of mass. In the limit of large r, the contribution of ϱ is negligible; because of Eq. (30), $Z(M_1/M)$ of the electrons are located near nucleus 1, with $\zeta = r(M_2/M)$, while $Z(M_2/M)$ electrons are near nucleus 2, with $\zeta = r(M_1/M)$. We thus have:

$$\frac{\langle \zeta^2 + \frac{1}{2}\varrho^2\rangle}{r^2} = \frac{\langle \zeta^2\rangle}{r^2} = Z\left\{\frac{M_1}{M}\left(\frac{M_2}{M}\right)^2 + \frac{M_2}{M}\left(\frac{M_1}{M}\right)^2\right\} = Z\frac{\mu}{M}. \tag{52}$$

Inserting this into Eq. (51), one obtains in this limiting case:

$$\hat{H}^{\mathrm{nuc}}_{\mathrm{geom}} = \frac{Ze\hbar}{2Mc}\boldsymbol{B}\cdot\hat{\boldsymbol{L}}, \tag{53}$$

which, as we would expect, just cancels the magnetic term in Eq. (32). For finite internuclear distances, the cancellation is not exact, but just represents the electronic contribution (in Born–Oppenheimer approximation) to the magnetic moment of the molecule.

The geometric phase thus accounts for the intuitively expected correction to the molecular magnetic moment due to the electron cloud following the nuclear motion. Like the result of the preceding station, this result is hardly surprising, but it does not come out of a Born–Oppenheimer treatment without inclusion of the geometric phase.

5. Discussion

We have seen that the correct treatment of the geometric vector potential induced by an external magnetic field is capable of correcting an annoying defect in the usual Born–Oppenheimer approach, namely that the external field appears to interact with bare nuclei. With inclusion of the geometric potential, the external field "sees" the entire molecule, including the negatively-charged electronic cloud. Of course, there will be a correction also to the interaction of molecular vibrational motion with the external field, but this will be more difficult to evaluate, since vibrations distort the electronic cloud rather than just translating or rotating it. Nevertheless, our general approach should be capable of dealing with corrections to the interaction of vibrations with the external field, and we hope to take this up in a future publication. One expects modifications of magnetic moments associated with vibrations, which will be attributable to the electronic cloud partially following the nuclear motion.

The effect calculated here is not to be confused with the actual effect on the nuclei of the magnetic field of the electrons [12]. We have not included in our hamiltonian any term corresponding to the ability of electrons or nuclei to generate or influence magnetic fields. In particular, the correction that we calculate to the magnetic interaction does not appear to apply to the interaction of the nuclear spin with the magnetic field. The question of the spin interaction is not entirely trivial, however, and we also plan to take it up in a future publication.

Dedication. It is a pleasure to dedicate this article to our highly esteemed colleague Stephen Prager.

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Note added in proof. We have recently realized that Eq. (48), and its consequences (49) and (51), are exact only in the separated-atom limit. A more complete account will be published elsewhere.