

Ab Initio Calculation of the Vibrational Magnetic Dipole Moment

Petr Bour,^{*,†,‡} Cheok N. Tam,[†] and Timothy A. Keiderling^{*,†}

Department of Chemistry, University of Illinois at Chicago, M/C 111, 845 W. Taylor, Chicago, Illinois 60607-7061, and Institute of Organic Chemistry and Biochemistry, Academy of Sciences, Flemingovo nam 2, 16610, Prague, Czech Republic

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To theoretically explain the vibrational magnetic dipole moment of a molecule with degenerate vibrational levels, it is necessary to go beyond the Born–Oppenheimer approximation. To obtain a nonzero electronic contribution to the vibrational *g* factor, electronic excited states must be included. Moreover, the usual perturbation expression for the vibrational magnetic moment becomes zero for degenerate vibrational states, unless higher order perturbation terms are included. For ab initio computation of these magnetic moments two simplified models have been tested by calculating the molecular *g* factors for the C₂H₂, HCN, OCS, and NH₃ molecules and comparing them to experimental values.

Introduction

If the Born–Oppenheimer (B–O) approximation is used for calculation of the molecular ground state magnetic properties, the electronic contributions to the magnetic dipole moment vanish for real electronic wave functions.¹ However, the electronic contribution to the vibrational and rotational magnetic moment is of the same order as the nuclear part, which has been confirmed by numerous experiments including vibrational circular dichroism (VCD) measurements which depend on magnetic transition moments,² molecular Zeeman effect studies which yield rotational gyromagnetic ratios,³ or vibrational magnetic moments⁴ and, finally, by rotationally resolved magnetic VCD (RR MVCD) that allows measurement of both the rotational and vibrational magnetic moments.⁵

For calculation of the rotational magnetic moment, a perturbational formula was derived,^{6,7} allowing one to calculate the *g* factor from the paramagnetic part of the electronic susceptibility, which is available as an option in ab initio quantum chemical programs.⁸

Similarly, the magnetic field perturbation theory (MFP)⁹ allows a relatively simple calculation of the vibrational magnetic transition moment, since it is based on a perturbation of the electronic ground state. Recently, a common formalism was found, based on the MFP model, that allows one to express formally both the rotational and vibrational magnetic moments in terms of derivatives of the electronic ground state wave function with respect to the magnetic field.¹ Although originally developed for the harmonic approximation, this formalism can be used for a general vibrational wavefunction.¹⁰

For molecules with degenerate vibrational levels, the pure vibrational angular momenta in excited states and their associated magnetic moments can be observed, as shown for OCS,¹¹ HCN,¹¹ C₂H₂,⁵ and NH₃.⁴ For such a case, however, the first-order perturbational formula (see ref 1, eq 21) again gives no contribution from the electronic part. An expression for the electronic contribution has been derived for symmetric top molecules.¹² An alternative view of the electronic contribution has been proposed using a parametrized vibrational–electronic coupling scheme recently computationally implemented on a semiempirical level for a calculation of vibrational magnetic moments in high symmetry (mostly aromatic) polyatomics.¹³

In this paper, we will discuss a nonadiabatic expression for potential evaluation of the electronic vibrational magnetic moment. In addition, we propose a dipole derivatives-based model that provides a means for practical calculation of these magnetic moments. Calculated results using it are compared to those from the rotational model for linear molecules, put forth in ref 12.

Theory

The magnetic dipole moment operator can be written as a sum of the nuclear and electronic contributions:

$$\mathbf{m} = \mathbf{m}_n + \mathbf{m}_e = \sum_{\lambda=1}^N \frac{Z_{\lambda}e}{2M_{\lambda}} \mathbf{r}^{\lambda} \times \mathbf{p}^{\lambda} - \frac{e}{2m_e} \sum_{i=1}^{N_e} \mathbf{r}^i \times \mathbf{p}^i \quad (1)$$

where $Z_{\lambda}e$ and M_{λ} are the charge and mass of a nucleus λ , while $(-e)$ and m_e are the charge and mass of the electron. The radius vectors of the nuclei (λ) and electrons (i) are denoted by \mathbf{r}^{λ} and \mathbf{r}^i , respectively. The conjugate momenta are similarly denoted as \mathbf{p}^{λ} and \mathbf{p}^i . N is the number of atoms, and N_e is the number of electrons.

The nuclear part can be obtained directly. Undergoing vibrational motion in a normal mode, l , the nuclei move along the normal mode coordinates, Q_l , causing a deviation $\Delta\mathbf{r}^{\lambda}$ from their equilibrium positions $\mathbf{r}^{\lambda,0}$, so that, for the α -coordinate

$$\mathbf{r}_{\alpha}^{\lambda} = \mathbf{r}_{\alpha}^{\lambda,0} + \Delta\mathbf{r}_{\alpha}^{\lambda} = \mathbf{r}_{\alpha}^{\lambda,0} + \sum_l \mathbf{S}_{\alpha,l}^{\lambda} Q_l$$

where \mathbf{S} is the normal-mode transformation matrix into Cartesian coordinates (denoted by Greek letters). Similarly, the nuclear momenta, \mathbf{p}^{λ} , can be obtained from the normal mode momenta, P_l , as $p_{\alpha}^{\lambda} = M_{\lambda} \sum_l \mathbf{S}_{\alpha,l}^{\lambda} P_l$. Combining these with eq 1, the nuclear magnetic moment is given by

$$m_{n,\alpha} = \sum_{\lambda=1}^N \frac{Z_{\lambda}e}{2} \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} (\mathbf{r}_{\beta}^{\lambda,0} \sum_l \mathbf{S}_{\gamma,l}^{\lambda} P_l + \sum_{l,k} \mathbf{S}_{\beta,l}^{\lambda} \mathbf{S}_{\gamma,k}^{\lambda} Q_l P_k) \quad (2)$$

For an observable vibrational magnetic moment, however, only the second expression in this equation survives, since $\langle v | \mathbf{P}_l | v \rangle = 0$ for any vibrational state v . Indeed, at least two normal

[†] University of Illinois at Chicago.

[‡] Academy of Sciences.

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mode motions must be combined to yield a nonzero molecular angular momentum.

The electronic part of the magnetic moment is given by the matrix element

$$\langle m_{e,\alpha} \rangle = \langle v | \langle \psi_G' | \mathbf{m}_{e,\alpha} | \psi_G' \rangle | v \rangle \quad (3)$$

where $v(r^i)$ is the vibrational wave function and ψ_G' is a perturbed (non-B-O) electronic ground-state wave function. The perturbation arises from the motion of nuclei and can be obtained from the kinetic energy matrix element using electronic wave functions $\langle \psi_{K'} | T | \psi_{K'} \rangle$; for B-O electronic wave functions, $\langle \psi_K | T | \psi_K \rangle = T \delta_{K,K'}$. Such a nonadiabatic treatment would address the problem of interest but, in our hands, is not computationally realizable at present. According to our previous experience, we expect to obtain results of low accuracy, if a second-order perturbational calculation is performed using an incomplete basis set. The vibronic coupling based formalism of Pawlikowski¹³ approaches this problem using a diabatic basis for a limited set of states and an unitary transformation to reduce off-diagonal terms in the perturbation. Here, as an alternative approach, we develop below a computationally inexpensive model that can be used for approximate calculations of vibrational magnetic moments.

Polarization Model. Eventually, it will be convenient to obtain the electronic contribution to the magnetic moment as a sum over nuclei. Let us write the electric dipole moment change as

$$\Delta \mu_\beta = \sum_{\alpha,\lambda} P_{\alpha\beta}^\lambda \Delta r_\alpha^\lambda = \sum_{\alpha,\lambda} Z_\lambda e \delta_{\beta\alpha} (\Delta r_\alpha^\lambda - \Delta r_\alpha^{e,\lambda}) \quad (4)$$

where P is the atomic polar tensor,⁹ which can be calculated with a high precision by most quantum chemistry programs; $\delta_{\beta\alpha}$ is a Kronecker delta, and $\Delta r^{e,\lambda}$ is a new parameter to represent a classical effective electron path correlated to the nuclear motion. Note that if a cloud of electrons of the charge Z_λ followed the nuclear shift exactly, i.e., $\Delta r^{e,\lambda} = \Delta r^\lambda$, then $\Delta \mu = 0$. Using the definition of normal modes, we reexpress our electron path parameter as

$$\Delta r_\alpha^{e,\lambda} = \sum_\beta (\delta_{\alpha\beta} - P_{\beta\alpha}^\lambda (Z_\lambda e)^{-1}) \Delta r_\beta^\lambda = \sum_{\beta,i} (\delta_{\alpha\beta} - P_{\beta\alpha}^\lambda (Z_\lambda e)^{-1}) S_{\beta,i}^\lambda Q_i \quad (5a)$$

Correspondingly, its conjugate momentum can be expressed in terms of its time derivatives, $\Delta \dot{r}_\alpha^{e,\lambda}$, as

$$p_\alpha^{e,\lambda} = m_{e1} \Delta \dot{r}_\alpha^{e,\lambda} = m_{e1} \sum_{\beta,i} (\delta_{\alpha\beta} - P_{\beta\alpha}^\lambda Z_\lambda^{-1}) S_{\beta,i}^\lambda \dot{P}_i \quad (5b)$$

Finally, the electron contribution to the magnetic moment can be written in terms of an effective electron cloud angular momentum summed over the clouds, rather than over individual electrons:

$$m_{e,\alpha} = - \frac{e}{2m_{e1}} \sum_\lambda \epsilon_{\alpha\beta\gamma} \Delta r_\beta^{e,\lambda} p_\gamma^{e,\lambda} \quad (6)$$

with Δr^i and p^i given by eqs 5a and 5b, respectively. Note that due to the parametrization being dependent on the overall atomic polar tensor, the electron clouds do not have to be localized in space and that, in terms of our definition (eq 4), the sum over clouds is equivalent to a sum over nuclei.

Degenerate Vibrational States. To apply this to the special case of the singly excited degenerate vibrational state, consider vibrational wavefunctions for the two dimensional isotropic harmonic oscillator:

$$|\pm\rangle = (1/\sqrt{2})(|1a\rangle|0b\rangle \pm i|0a\rangle|1b\rangle) \quad (7)$$

Here the c axis is the molecular axis of highest symmetry, $1a$ and $1b$ correspond to the single quantum excitation of the vibrational modes polarized along the symmetry equivalent a and b axes. The nuclear (n) and electronic (e) magnetic moments are then

$$\langle \pm | m_{n/e,\alpha} | \pm \rangle = \pm m_{n/e,\alpha,a,b} \hbar \quad (8)$$

where $m_{n/e,\alpha,a,b} = -m_{n/e,\alpha,b,a}$. Substituting eqs 2 and 6 for the nuclear and electronic magnetic moments, respectively, we get

$$m_{n,\alpha,a,b} = \sum_{\lambda=1}^N \frac{Z_\lambda e}{2} \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} S_{\beta,a}^\lambda S_{\gamma,b}^\lambda \quad (9a)$$

$$m_{e,\alpha,a,b} = -(1/2) \sum_{\lambda,\beta,\gamma} \epsilon_{\alpha\beta\gamma} (Z_\lambda e) S_{\beta,a}^\lambda S_{\gamma,b}^\lambda + (Z_\lambda e)^{-1} \sum_{\sigma,\epsilon} P_{\sigma\beta}^\lambda P_{\sigma\epsilon}^\lambda S_{\sigma,a}^\lambda S_{\epsilon,b}^\lambda - \sum_{\sigma} P_{\sigma\beta}^\lambda S_{\sigma,a}^\lambda S_{\gamma,b}^\lambda - \sum_{\sigma} P_{\sigma\gamma}^\lambda S_{\beta,a}^\lambda S_{\sigma,b}^\lambda \quad (9b)$$

The vibrational angular momentum is approximately equal to the nuclear contribution, $l = l_n + l_e \approx \sum_{\lambda=1}^N r^\lambda \times p^\lambda$, and the matrix element would be

$$\langle \pm | l_{n,\alpha} | \pm \rangle = \pm l_{n,\alpha,a,b} \hbar \quad (10)$$

where

$$l_{n,\alpha,a,b} = \sum_{\lambda=1}^N M_\lambda \sum_{\beta\gamma} \epsilon_{\alpha\beta\gamma} S_{\beta,a}^\lambda S_{\gamma,b}^\lambda \quad \text{and} \quad l_{e,\alpha,a,b} = -l_{n,\alpha,b,a}$$

The vibrational quantum number corresponds to a proper molecular rotation for linear molecules only. Generally, its contribution to the measurable molecular angular momentum is defined by the Coriolis coupling parameter.⁴ In accordance with earlier definitions, we define the vibrational g factor independently of the coupling parameter, as

$$g_v = g_{v,n} + g_{v,e} = \frac{\hbar[|m_{n,a,b}| + |m_{e,a,b}|]}{\mu_N |l_{n,a,b}|} \quad (11)$$

where μ_N is the nuclear magneton.

Rotational Model. As has been pointed out,^{11,12} for a linear molecule the vibrational g value is equal to the rotational g value for the molecular axis, if the molecule is slightly distorted according to the degenerate vibrational mode. As an alternate derivation, one needs to realize that in the first approximation the magnetic and angular momenta associated with the bending modes are proportional to the *square* of the deviation from the axis, and hence their ratio, the g value, is independent of the actual deviation to first order. The g_{zz} factor (z is the molecular axis) can then be obtained as

$$g_v = g_{zz} = (M_P / I_{zz}) \left(\sum_\lambda Z_\lambda ((r_x^\lambda)^2 + (r_y^\lambda)^2) - \frac{4m_e c^2}{e^2} \chi_{zz}^{e,PARA} \right) \quad (12)$$

TABLE 1: Ab Initio Calculations of the Vibrational g Factor

molecule/mode	calculation	polarization model $g_v(g_n + g_e)$	rotational model $g_v(g_n + g_e)$	experiment
C_2H_2/ν_5^a	HF/4-31G	0.405(0.961 - 0.559)	0.747(0.961 - 0.213)	0.48(25) ^c
	HF/6-31G**	0.358(0.961 - 0.602)	0.565(0.961 - 0.395)	
	HF/spd	0.384(0.961 - 0.577)	0.440(0.961 - 0.521)	
	MP2/6-31G**	0.356(0.961 - 0.605)		
HCN	HF/6-31GE	0.35(0.88 - 0.52)	0.51(0.86 - 0.35)	0.38(6) ^d
	HF/spd	0.33(0.86 - 0.53)		
	MP2/6-31GE	0.34(0.87 - 0.53)		
	QCISD/CEP ^b	0.34(0.86 - 0.53)		
OCS	HF/6-31GE	0.030(0.504 - 0.474)	0.161(0.504 - 0.343)	0.061(2) ^d
	HF/spd	0.033(0.504 - 0.471)		
	QCISD/CEP ^b	0.020(0.504 - 0.483)		
NH_3/ν_4	HF/6-31GE	0.86(1.38 - 0.52)		0.95(05) ^e
	MP2/6-31GE	0.57(1.12 - 0.55)		
	MP2/spd	0.63(1.12 - 0.49)		
NH_3/ν_3	QCISD/CEP	0.59(1.12 - 0.52)		
	HF/6-31GE	-0.30(0.05 - 0.35)		
	MP2/6-31GE	-0.42(-0.23 - 0.18)		
	MP2/spd	-0.39(-0.14 - 0.24)		
	QCISD/CEP	-0.32(-0.16 - 0.17)		

^a Experimental geometry was used. ^b Experimental geometry;⁷ for other calculations the energy minimum geometry was used. ^c Reference 5a. ^d Reference 11. ^e Reference 4.

where M_P is the proton mass, c is the velocity of light, I_{zz} is the moment of inertia, and $\chi_{zz}^{e,PARA}$ is the electronic part of the paramagnetic susceptibility.⁷

Results and Discussion

The dipole derivatives (atomic polar tensor) were estimated at the HF level and again using the MP2 and QCISD methods which include part of the correlation energy. The susceptibility evaluation needed in the rotational model was calculated at the HF level only. Basis sets used include the extended 6-31G basis set (two sets of polarization functions added) and the spd basis which includes the 8s6p basis on heavy atoms and 6s basis on hydrogens plus polarization functions, both as defined in the Cadpac program package.⁸ In addition, the QCISD calculations used the CEP basis, a triple split-valence basis set with polarization functions, as supplied in the Gaussian package.¹⁵ The QCISD second derivatives were calculated by numerical differentiation of the gradients, using the Gaussian 92 program. The Cadpac⁸ and Gaussian 92¹⁵ programs were used for the ab initio calculations of the g_v values yielding results with different basis sets, as summarized in Table 1.

For C_2H_2 we see a much weaker basis set dependence of the calculated g factor for the polarization model than for the rotational model. This might have been expected, since a much larger basis set is needed for a reliable calculation of the susceptibility, which is required in the latter method, because in that case the gradient of the electronic wave function is explicitly included in the calculation. All the calculations agree with the experimental g factor within its error limits, which, however, are quite large.

For HCN, the polarization model yields a reasonable estimate of the experimental g value, exact within its more reasonable experimental error bars, while the rotational model overestimates the g factor by about 30%.

For OCS, the agreement of the calculations with experiment is less satisfying, in terms of the relative error. Clearly, being small, the calculated g value is exceptionally sensitive to the accuracy of the estimation of the electronic contribution. The polarization model yields a more realistic value for the g factor, but one underestimated by about 50%, than does the rotational model calculation via magnetic susceptibility whose values is much too high.

Errors of 20–30% characterize the computed g values for the ν_4 mode of ammonia which are all lower than the

experimental value. Here the sources of errors cannot be clearly separated and include the anharmonic effects as well as errors in calculated geometries and normal modes. Clearly, the calculated value is 2–3 times larger than those calculated for the HCN or C_2H_2 molecules, in accordance with experimental data. For the ammonia ν_4 mode, the Zeeman energy splitting is also strongly influenced by the Coriolis coupling term, in addition to the g value. The Coriolis coupling parameter was calculated to be 0.25 from the MP2/spd and QCISD calculations, which is a very good representation of the experimental value of 0.24.⁴

Quite an interesting result was obtained for the ν_3 N–H stretching mode of ammonia, where both the nuclear and electronic g factors are calculated to be negative. In undergoing this motion, the NH_3 nuclear angular momentum points in the opposite direction from the nuclear magnetic moment. Measurable magnetic and angular momenta are small for this mode, the Coriolis coupling constant was calculated as 0.035 for the MP2 and QCISD calculations. Unfortunately, an experimental value of g_v is not available.

While the polarization model is clearly able to estimate the approximate magnitudes and signs of the vibrational g factors of the molecules studied here, there is an intrinsic limit to its accuracy, given by the approximations described above. Using post-HF procedures does not improve the results significantly, as shown for the HCN, OCS, and NH_3 molecules, and further work will be needed to improve the accuracy in order to completely account for the experimental magnetic moments.

Conclusions

A rigorous analytical calculation of the vibrational magnetic moment would have to include a sum over excited electronic states to go beyond the B–O approximation as a correction for the adiabatic electronic contribution, which is zero. We have found that the polarization model, based on the electric dipolar derivatives, works reasonably well for the systems studied. Also, the rotational model can be used for calculation of the g value for linear molecules, although its implementation requires a use of a relatively large basis set to get reasonable results.

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Appendix

The perturbational operator form of the B–O Hamiltonian can be obtained as

$$V = i\hbar \sum_{K,\alpha} \{ |\psi_K\rangle \langle \phi_{K,\alpha} | P_\alpha + \sum_{\beta} |\phi_{K,\alpha}\rangle \langle \phi_{K,\beta} | (R_\alpha P_\beta - P_\alpha R_\beta) + (1/2) \sum_{\beta} (|\psi_K\rangle \langle \theta_{K,\alpha\beta} | R_\alpha P_\beta - |\theta_{K,\alpha\beta}\rangle \langle \psi_K | P_\beta R_\alpha) \} \quad (A1)$$

where R_α is a mass-weighted nuclear displacement ($[R_\alpha, T] = i/\hbar P_\alpha$) and a Taylor expression of the electronic wave functions about the equilibrium geometry was used in the form $\psi_K' = \psi_K + \sum_{\alpha} \phi_{K,\alpha} R_\alpha + (1/2) \sum_{\alpha\beta} \theta_{K,\alpha\beta} R_\alpha R_\beta$. All terms in eq A1 must be kept to obtain the correct electronic contribution to the vibrational magnetic moment. Computationally, this would be a difficult procedure due to the inclusion of the sums over excited electronic states.

As an alternative point of view, we can consider the coordinate dependence of the electronic part of the atomic axial tensor, $I_{\beta\alpha} = -\langle \chi_{G,\alpha} | \phi_{G,\beta} \rangle$, where $\chi_{G,\alpha} = [(\partial/\partial \mathbf{B}_\alpha) \psi_K]_{\mathbf{B}=0}$, and \mathbf{B} is the magnetic field strength. Considering P_α and R_α as independent variables (as we should in Hamilton's formalism), we obtain

$$\langle \psi_G | \mathbf{m}_{e,\alpha} | \psi_G \rangle = -2i\hbar \sum_{\beta} \{ I_{\beta\alpha} P_\beta + (\partial I_{\beta\alpha} / \partial R_\gamma) R_\gamma P_B \} \quad (A2)$$

In this form, we can see that the second ("anharmonic") derivative of the magnetic moment according to the nuclear

coordinates ($\partial I_{\beta\alpha} / \partial R_\gamma$), is responsible for the electronic contribution to the purely vibrational magnetic moment.

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