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Paramagnetism in Closed-Shell Molecules

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Proofs that closed-shell molecules must be diamagnetic are shown to be restricted to two-electron systems. An exact nonrelativistic ground-state wave function having four or more electrons is shown to possess a nodal structure which arises from the Pauli principle. These nodes cause the proofs that a closed-shell molecular wave function is necessarily diamagnetic to be invalid when more than one pair of electrons is present. The physical situation is examined with special reference to the diatomic BH molecule.

I. INTRODUCTION

Practically everyone knows that most closed-shell molecules are diamagnetic. Both electron spin and electron orbital angular momenta are oppositely paired, so that no permanent moment remains for alignment by an external magnetic field.[1] The field must create a moment due to electronic currents, induced according to Larmor's theorem (or Lenz's law), in a direction which produces a force opposing introduction of the molecule into the magnetic field.[2] These effects are temperature-independent, and some orders of magnitude smaller than the temperature-dependent paramagnetic effects when a permanent magnetic moment is present. While this relatively small diamagnetic effect dominates the magnetic susceptibilities of most closed-shell species, careful measurements have yielded evidence in some complex salts[3] for the existence of a weak temperature-independent paramagnetism.

Van Vleck[1,4] developed a perturbation theory for the molar susceptibility χ of an N-electron molecule in its nth electronic state with energy E_n. His result is

$$\chi/N_0=\frac{\mu^2}{3kT}+\frac{2}{3}\sum_{n'(\neq n)}(E_{n'}-E_n)^{-1}\,|\,(n\,|\sum_{i=1}^{N}m_i^0\,|\,n')\,|^2-\frac{e^2}{6mc^2}(n\,|\sum_{i=1}^{N}r_i^2\,|\,n),\quad(1)$$

where N_0 is Avogadro's number, $\boldsymbol{\mu}$ is the permanent molecular magnetic dipole moment, and $\mathbf{m}_i^0=-(e/2mc)(\mathbf{L}_i+2\mathbf{S}_i)$ is the instantaneous magnetic dipole moment of the ith electron at $\mathbf{r}_i$ possessing orbital angular momentum $\mathbf{L}_i$ and spin angular momentum $\mathbf{S}_i$ in the absence of a magnetic field. We shall not consider open-shell systems which require the first term, describing temperature-dependent paramagnetism; this first term, when present, is a few orders of magnitude larger than the other terms. For a closed-shell molecule[5] ($\boldsymbol{\mu}=0$) in its ground electronic state ($n=0$), the second term is positive representing the temperature-independent paramagnetic susceptibility $\chi^{(p)}$, and the third term is negative representing the diamagnetic susceptibility $\chi^{(d)}$. Thus the unusual examples[3] of temperature-independent paramagnetism arise when $|\chi^{(p)}|>|\chi^{(d)}|$. Theoretical support for these unusual experimental examples is lacking, because Eq. (1) requires wave functions for all electronic states, including the continuum, for these complexes.[6]

Recently, Guy, Tillieu, and Baudet[7] have presented a proof that $\chi^{(p)}$ cannot be larger in absolute magnitude than $\chi^{(d)}$ for closed-shell molecular systems, and hence that these systems are *necessarily* diamagnetic. This proof, discussed below, is based upon Van Vleck's theory and the variation principle. These investigators then conclude that the explanation of temperature-independent paramagnetism is to be sought elsewhere. Rebane[8] gave a similar proof in a one-electron treatment, in which the perturbing operators were expressed as functions of the magnetic vector potential, and a gauge more flexible than that used by Van Vleck was chosen. Rebane did find a gauge transformation[9] which caused $\chi^{(p)}$ to vanish, thus demonstrating that the total susceptibility is diamagnetic, but he pointed out that his proof failed if the one-electron function had nodal surfaces. Thus, he concluded[8] that his results applied

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[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

[2] It should be recalled that if there is more than one nucleus Larmor's theorem does not strictly apply. However, it is common to speak of a "diamagnetic circulation hindered by the bonds" when considering the electronic currents induced in a molecule. See also Ref. 1, p. 90.

[3] (a) T. Ishiwara, Sci. Rept. Tohoku Univ. **3**, 303 (1914); (b) E. Rosenbloom, Z. Phys. Chem. **93**, 693 (1919); (c) P. Wein and P. Collet, Compt. Rend. **178**, 2146 (1924), **181**, 1051 (1925); **182**, 105 (1926); (d) S. Berkman and H. Zocher, Z. Phys. Chem. **124**, 318 (1926); (e) R. Ladenburg, Z. Phys. Chem. **126**, 133 (1927); (f) S. Freed and C. Kasper, J. Am. Chem. Soc. **52**, 4671 (1930); (g) W. Gray and J. Dakers, Phil. Mag. **11**, 297 (1931); (h) W. R. Angus, Proc. Roy. Soc. (London) **A136**, 579 (1932); (i) P. Henkel and W. Klemm, Z. Anorg. Chem. **222**, 71 (1935); (j) D. P. Raychandhuri and P. N. Sengupta, Indian J. Phys. **10**, 245 (1936); (k) See also J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, New York, 1961), p. 278ff. for an approximate theoretical treatment.

[4] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927); **30**, 31 (1927); **31**, 587 (1928).

[5] Nuclear spins and molecular rotation also make small contributions to the susceptibility, but these effects are neglected here. See Ref. 1, p. 259 and Footnote 34 on p. 277.

[6] More recently a semi-empirical calculation of the susceptibility of the paramagnetic closed-shell ion MnO_4^- has been attempted on the basis of Van Vleck's formula. See A. Carrington, Mol. Phys. **3**, 271 (1960).

[7] J. Guy, J. Tillieu, and J. Baudet, Compt. Rend. **246**, 574 (1958); J. Tillieu, Ann. Phys. (Paris) **2**, 471 (1957).

[8] T. K. Rebane, Zh. Eksperim. i Teor. Fiz. **38**, 963 (1960) [English transl.: Soviet Phys.—JETP **11**, 694 (1960)].

[9] H. F. Hameka, *Advanced Quantum Chemistry* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1965), Chap. 9.

only to the ground state. This point has been discussed briefly by other authors.[10]

Confusion still exists,[11] therefore, as to whether or not theory permits a closed-shell molecule to be paramagnetic. One facet of this problem is the interpretation of molecular rotational magnetic moments g_λ in terms of electron "slippage."[12] For rigid body (RB) rotation (no electron slippage) of a diatomic molecule about an axis λ, there is a nuclear contribution N_λ and an electronic contribution[12–14] to the rotational g factor,

$$g_\lambda^{\mathrm{RB}}=N_\lambda+K_\lambda\chi_{\lambda\lambda}^{(d)}, \tag{2}$$

where K_λ is a constant for the molecule. On the other hand, if perturbations to the rigid body rotation are included, the relation to susceptibility is

$$g_\lambda=N_\lambda-K_\lambda\chi_{\lambda\lambda}^{(p)}. \tag{3}$$

The usual interpretation when $g_\lambda>g_\lambda^{\mathrm{RB}}$ is that electron slippage has reduced the electronic contribution from the rigid body value, thus resulting in a more positive g value.[15] Now, if a closed-shell molecule could be paramagnetic we would have $g_\lambda<g_\lambda^{\mathrm{RB}}$. Shall we call this effect "anti-slippage"? At least, the meaning of this concept needs to be clarified. At most, the possible presence of weak temperature-independent paramagnetism would lead us to suspect the interpretation of the slippage concept.

Accordingly, we felt that the theoretical possibility of temperature-independent paramagnetism in closed-shell molecules should be reinvestigated. In Sec. II, Rebane's formulation is generalized to N-electron wavefunctions for closed-shell systems, and the results are then related to ordinary perturbation theory. In this section, as well as in Sec. III, where relations are developed between the approaches of Rebane and of Guy *et al.*, we see that the proofs of the relation $\chi\leq 0$ for the N-electron case are not valid if the wave function has nodal surfaces. This is a generalization from the one-electron systems considered by Rebane. In Sec. IV we show that the Pauli principle introduces nodal surfaces into a ground state N-electron wave function when $N>2$, and hence it is *not impossible* for a closed-shell molecule having four or more electrons to be paramagnetic. Finally, the interpretation of this net paramagnetism is discussed in Sec. V.

II. REBANE APPROACH WITH MANY-ELECTRON WAVE FUNCTIONS

In a manner parallel to Rebane's treatment of a single electron,[8] one may express the energy change due to a uniform magnetic field H of arbitrary (fixed) direction with respect to a closed-shell N-electron molecule in its ground state Ψ_0

$$\Delta E=\frac{e^2}{2mc^2}(\Psi_0\mid\sum_{k=1}^{N}A_k^2\mid\Psi_0)-\frac{e^2\hbar^2}{m^2c^2}\sum_{n\neq0}(E_n-E_0)^{-1}\times\mid(\Psi_n\mid\sum_{k=1}^{N}\mathbf{A}_k\cdot\nabla_k+\tfrac{1}{2}\nabla_k\cdot\mathbf{A}_k\mid\Psi_0)\mid^2, \tag{4}$$

where

$$\mathbf{A}_k=\mathbf{A}_{0k}+\nabla_k f(1\cdots N) \tag{5}$$

is the vector potential for the kth electron, $\nabla_k\times\mathbf{A}_k=\mathbf{H}$, $\nabla_k\cdot\mathbf{A}_{0k}=0$, and $f(1\cdots N)$ is an arbitrary scalar function of the space and spin coordinates of the N electrons. The eigenfunctions Ψ_n are solutions of $\mathcal{H}_0\Psi_n=E_n\Psi_n$ for $\mathcal{H}_0$, the Hamiltonian for the field-absent case. The susceptibility is found by employing the relation

$$\Delta E=-\chi H^2/2N_0. \tag{6}$$

Although ΔE is invariant with respect to the choice for f, each term in (4) depends upon this choice. In particular if f satisfies the equation

$$\tfrac{1}{2}\sum_{k=1}^{N}\nabla_k^2 f+\sum_{k=1}^{N}\nabla_k f\cdot\nabla_k\Psi_0+\sum_{k=1}^{N}\mathbf{A}_{0k}\cdot\nabla_k\Psi_0=0 \tag{7}$$

the second term in (4) vanishes and the energy change becomes

$$\begin{aligned}\Delta E&=\frac{e^2}{2mc^2}(\Psi_0\mid\sum_{k=1}^{N}(A_{0k}+\nabla_k f)^2\mid\Psi_0),\\&=\frac{e^2}{2mc^2}(\Psi_0\mid\sum_{k=1}^{N}(A_{0k}^2+\mathbf{A}_{0k}\cdot\nabla_k f)\mid\Psi_0),\\&=\frac{e^2}{2mc^2}(\Psi_0\mid\sum_{k=1}^{N}(A_{0k}^2-\nabla_k f\cdot\nabla_k f)\mid\Psi_0),\end{aligned} \tag{8}$$

where the last two lines of (8) were obtained after multiplying (7) by $f\Psi_0$ and integrating. The first line of (8) shows that the molecule must be diamagnetic if a solution to (7) exists. Following Rebane, we may express this solution[16]

$$f(1\cdots N)=\frac{\hbar^2}{m}\sum_{n\neq0}(E_n-E_0)^{-1}(\Psi_n\mid\sum_{k=1}^{N}\mathbf{A}_{0k}\cdot\nabla_k\mid\Psi_0)\times[\Psi_n(1\cdots N)/\Psi_0(1\cdots N)]. \tag{9}$$

However, we see immediately that f becomes infinite in regions where Ψ_0 possesses nodal surfaces not identical to those of Ψ_n, resulting in the possible divergence of integrals in (8). As Rebane has pointed out,[8] the existence of these integrals is essential to the proof of

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[10] A. D. McLachlan and M. R. Baker, Mol. Phys. **4**, 255 (1961). See also Ref. 24, below.

[11] Compare Refs. 7–10 for example, and see also A. D. McLean and M. Yoshimine, J. Chem. Phys. **45**, 3676 (1966).

[12] G. C. Wick, Z. Physik **85**, 25 (1933).

[13] G. C. Wick, Nuovo Cimento **10**, 118 (1933).

[14] J. R. Eshback and M. W. P. Strandberg, Phys. Rev. **85**, 24 (1952); W. Weltner, J. Chem. Phys. **28**, 477 (1958).

[15] It is commonly assumed that slippage occurs to some degree in all rotating molecules. See, e.g., Ref. 11.

[16] We have chosen to obtain $f(1\cdots N)$ as a function of the spin variables as well as of the spatial coordinates. Alternately, one could sum over the spin variables in (4) before obtaining the equation corresponding to (7).

the inequality $\Delta E \geq 0$. The problem thus becomes one of examining the nodal structure of the solutions of the N-particle Schrödinger equation for the molecule in the absence of the field. We return to this problem in Sec. IV.

Let us now examine the relationship of this gauge transformation theory to ordinary perturbation theory. In the latter method, we find for the second-order energy

$$\Delta E = (\Psi_0 \mid \mathcal{H}^{(2)} \mid \Psi_0) + (\Psi_0 \mid \mathcal{H}^{(1)} \mid \Psi^{(1)}), \tag{10}$$

where

$$\mathcal{H}^{(2)} = \frac{e^2}{2mc^2} \sum_{k=1}^{N} A_{0k}^2,$$

$$\mathcal{H}^{(1)} = \frac{e\hbar}{imc} \sum_{k=1}^{N} \mathbf{A}_{0k} \cdot \boldsymbol{\nabla}_k, \tag{11}$$

and where $\Psi^{(1)}$ is the solution of the equation

$$\Psi^{(1)} = -(\mathcal{H}_0 - E_0)^{-1} \mathcal{H}^{(1)} \Psi_0. \tag{12}$$

Note that here we restrict the vector potential to the Coulomb gauge. By expanding $\Psi^{(1)}$ in solutions of the zeroth-order Schrödinger equation

$$\Psi^{(1)} = \sum_n b_n \Psi_n \tag{13}$$

we obtain the usual equations for b_n

$$b_n = -\frac{e\hbar^2}{ic\hbar m} (E_n - E_0)^{-1} (\Psi_n \mid \sum_{k=1}^{N} \mathbf{A}_{0k} \cdot \boldsymbol{\nabla}_k \mid \Psi_0). \tag{14}$$

By comparison with (9) and (13) we see that the two methods are related through the expression

$$\Psi^{(1)} = (ie/\hbar c) f \Psi_0 \tag{15}$$

and that f will have singularities if Ψ_0 possesses nodes which are moved by the operator $\mathcal{H}^{(1)}$. A similar behavior in the case of one-electron functions was noted by investigators concerned with perturbations to molecular orbitals.[17]

III. VARIATION METHOD

The $\chi \leq 0$ proof of Guy, Tilleu, and Baudet[7] (GTB) rests upon the ability to reduce to a special simple form the variationally minimized expression for

$$E = (\Psi \mid \Psi)^{-1} (\Psi \mid \mathcal{H} \mid \Psi), \tag{16}$$

where

$$\Psi = [1 + (eH/2i\hbar c) G_u] \Psi_0$$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1; \; \mathcal{H}_0 \Psi_0 = E_0 \Psi_0$$

$$\mathcal{H}_1 = \frac{eH}{2mc} \sum_{k=1}^{N} L_{ku} + \frac{e^2H^2}{8mc^2} \sum_{k=1}^{N} (r_k^2 - u_k^2), \tag{17}$$

for a uniform magnetic field $\mathbf{H} = H\hat{\mathbf{u}}$ ($u = x$, y, or z) and for L_{ku} the u component of orbital angular momentum of electron k with spatial coordinate r_k. After substituting (17) into (16) and varying the function G_u to minimize E, one obtains the following equation for G_u:

$$\tfrac{1}{2}(i\hbar)\Psi_0 \sum_{k=1}^{N} \nabla_k^2 G_u + i\hbar \sum_{k=1}^{N} \boldsymbol{\nabla}_k G_u \cdot \boldsymbol{\nabla}_k \Psi_0 + \sum_k L_{ku} \Psi_0 = 0 \tag{18}$$

which may easily be shown to be identical to (7) after recalling $L_{ku} = (2\hbar/iH) \mathbf{A}_{0k} \cdot \boldsymbol{\nabla}_k$ thus relating this method to the Rebane method through the equation[18]

$$f = -(H/2) G_u. \tag{19}$$

Using (18), one obtains finally

$$E = E_0 + \frac{e^2H^2}{8mc^2} \sum_{k=1}^{N} (\Psi_0 \mid (r_k^2 - u_k^2) - 2\partial G_u/\partial\phi_{ku} + \boldsymbol{\nabla}_k G_u \cdot \boldsymbol{\nabla}_k G_u \mid \Psi_0) \tag{20}$$

or

$$E = E_0 + \frac{e^2H^2}{8mc^2} \sum_{k=1}^{N} (\Psi_0 \mid (r_k^2 - u_k^2) - \boldsymbol{\nabla}_k G_u \cdot \boldsymbol{\nabla}_k G_u \mid \Psi_0), \tag{21}$$

with $\partial/\partial\phi_{ku} = (i/\hbar) L_{ku}$. After comparison with (8) we see that the proof of GTB must be subject to the same limitations as that of Rebane, namely, the proof is not valid if Ψ_0 possesses nodal surfaces, a problem which we now consider.

IV. NODAL STRUCTURE OF GROUND-STATE ELECTRONIC WAVE FUNCTIONS

It has been pointed out previously that it is possible for a wave function corresponding to the stationary state of lowest energy of a system of several identical particles to possess nodes.[19] Indeed it is obvious that if two electrons have the same spin coordinate ($+\frac{1}{2}$ or $-\frac{1}{2}$) then because of the Pauli exclusion principle the spacial-coordinate part of the wave function must change sign upon an interchange of coordinates of the two electrons and vanish when these coordinates coincide. In addition to these "Fermi holes" there may be additional nodal structure, and it is this latter type of node we wish to investigate in more detail, since we see upon examining (9) that the existence of Fermi holes is not sufficient to cause the integrals in (8), (20), or (21) to diverge.

If we do not insist on the Pauli principle then it can be shown that the ground-state solution[20] $\psi^{(1)}$ of the

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[17] See Ref. 10; also M. Karplus and H. J. Kolker, J. Chem. Phys. **38,** 1263 (1963); M. Karplus and R. G. Parr, *ibid.* **38,** 1547 (1963); H. J. Kolker and M. Karplus, *ibid.* **41,** 1259 (1964).

[18] See also S. I. Chan and T. P. Das, J. Chem. Phys. **37,** 1527 (1962).

[19] See, for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958).

[20] Superscripts are used here to label energy eigenvalues, and are not to be confused with the superscripts of perturbation theory employed in earlier sections.

nonrelativistic Schrödinger equation

$$\mathcal{H}(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}) \tag{22}$$

is nodeless,[21] nondegenerate,[22] and for a symmetric Hamiltonian is completely symmetric[23] with respect to an interchange of the spatial coordinates $(\mathbf{r})=(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$ of any two electrons. In addition, since $[\mathcal{H}, P]=0$ for all permutations P of the N particles, every solution of (22) must belong to an irreducible representation of the permutation group $\mathcal{S}_N$. We may thus label these solutions according to their permutational symmetry: for $\psi^{(k)}$ a solution of (22),

$$\mathcal{H}\psi_n^{(k)}=E_k\psi_n^{(k)} \qquad n=1, \cdots, f^k$$

$$P\psi_n^{(k)}=\sum_{m=1}^{f^k}\psi_m^{(k)}\Gamma^{(k)}(P)_{mn}. \tag{23}$$

The eigenfunction corresponding to the lowest eigenvalue E_1 of (22) is nodeless and belongs to the one-dimensional totally symmetric representation of $\mathcal{S}_N$:

$$P\psi^{(1)}=\psi^{(1)} \tag{24}$$

for all P belonging to $\mathcal{S}_N$. All other eigenfunctions are orthogonal to $\psi^{(1)}$ and thus possess nodes.

Now the total, physically acceptable eigenfunctions of $\mathcal{H}$, which we denote by $\Psi_{SM_sE_k}(\mathbf{r}, \boldsymbol{\sigma})$, must be totally antisymmetric upon a simultaneous permutation of space and spin coordinates:

$$P^rP^\sigma\Psi_{SM_sE_k}=\epsilon_p\Psi_{SM_sE_k}, \tag{25}$$

where P^r, P^σ are, respectively, permutation operators acting on space and spin coordinates alone, and ϵ_p denotes the parity of P:

$$\begin{aligned}\epsilon_p&=+1, \qquad P \text{ even}\\ &=-1, \qquad P \text{ odd.}\end{aligned}$$

Furthermore, since the Hamiltonian $\mathcal{H}$ is not a function of the spin coordinates, and since the solutions of (22) transform according to (23) upon a perturbation P of the *spatial* coordinate, an *acceptable* physical state will be of the form

$$\Psi_{SM_sE_k}(\mathbf{r}, \boldsymbol{\sigma})=\sum_{n=1}^{f^k}\psi_n^{(k)}(\mathbf{r})\Theta_{SM_sn}(\boldsymbol{\sigma})$$

where the Θ_{SM_sn} are a set of spin eigenfunctions belonging to the irreducible representation *associated* with the $\psi_n^{(k)}$:

$$S^2\Theta_{SM_sn}=S(S+1)\Theta_{SM_sn},$$

$$S_z\Theta_{SM_sn}=M_s\Theta_{SM_sn},$$

$$P^\sigma\Theta_{SM_sn}=\sum_{m=1}^{f^k}\epsilon_p\Theta_{SM_sm}\Gamma^{(k)}(P)_{mn}. \tag{26}$$

For the lowest eigenfunction $\psi^{(1)}$, this implies that we must construct a set of spin functions that belong to the totally antisymmetric representation of $\mathcal{S}_N$:

$$P^\sigma\Theta_{SM_s1}(\boldsymbol{\sigma})=\epsilon_p\Theta_{SM_s1}(\boldsymbol{\sigma}).$$

But for $N>2$, this cannot be done since the spin variables $\boldsymbol{\sigma}$ can assume only two possible discrete values. Thus $\psi^{(1)}$, which is the only eigenfunction which is nodeless, must be rejected for $N>2$. Hence each acceptable eigenfunction, including that for the ground state which we have denoted Ψ_0, must have in addition to the Fermi holes the nodal structure of one of the higher eigenfunctions of (22).

V. DISCUSSION

We now see that the demonstrations that molecules are diamagnetic are valid only for molecules with less than three electrons. It is therefore reasonable to expect that the Van Vleck theory of magnetic susceptibilities can be employed to provide a basis for a theory of temperature-independent paramagnetism. The physical explanation for this effect in this theory is the unquenching of electronic orbital angular momentum in the molecule.[24,25] Consider, for example, the formation of a closed-shell diatomic molecule from two atoms each having a net spin and orbital angular momentum. As the atoms approach one another to form the molecule in its $^1\Sigma$ ground state (1) the electron spins become oppositely paired, (2) an additional orbital angular momentum is created due to exchange effects between

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[21] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 1, p. 452. See also B. W. Downs, Am. J. Phys. **31**, 277 (1963); T. Kato, Trans. Am. Math. Soc. **70**, 195 (1951); and E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (Dover Publications, Inc., New York, 1958), pp. 195–197, 215–217. Although the node theorem proved by Courant and Hilbert holds for any number of independent variables, there is some question as to whether it holds rigorously for unbounded potentials, i.e., the Coulomb interaction. Here we have essentially *assumed*, along with other authors,[19] that it does. It is evident, however, that our proof does not depend critically upon the statement that the lowest eigenfunction $\psi^{(1)}$ is nodeless; for if $\psi^{(1)}$ did indeed possess nodes, then these nodes would also be present in the physically acceptable state formed from $\psi^{(1)}$. The cardinal statement is that a physically acceptable eigenfunction $\Psi_{SM_sE_k}(\mathbf{r}, \boldsymbol{\sigma})$ cannot be formed from a nodeless $\psi^{(k)}(\mathbf{r})$ for $N>2$.

[22] If there existed two or more linearly independent eigenfunctions corresponding to the lowest eigenvalue, a linear combination of these functions could be chosen such that the resulting function was an eigenfunction still belonging to the lowest eigenvalue, but possessing nodes.

[23] Since $\mathcal{H}$ is symmetric, it commutes with any permutation P of the electrons, i.e., $[\mathcal{H}, P]=0$. Hence an eigenfunction, upon a permutation of its coordinates, remains an eigenfunction of $\mathcal{H}$ with the same eigenvalue. If the first eigenfunction $\psi^{(1)}$ were antisymmetric with respect to the interchange of the coordinates of any two electrons, however, this function would have a node wherever these coordinates coincided.

[24] Reference 1, pp. 276–279.

[25] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), Chap. 4.

the two atoms, (3) the electronic orbital angular momenta quantize appropriate to the molecular symmetry ($\Lambda=0$), and (4) the net orbital angular momentum perpendicular to the internuclear axis is quenched due to torques arising from the nonspherical nature of the molecular potential. This quenching is such that the average value of the total orbital angular momentum squared is nonvanishing although the expectation value of any component is zero. The total angular momentum of the free molecule is necessarily constant, but there are fluctuations between the electronic orbital angular momentum perpendicular to the internuclear axis and the angular momentum due to the molecular rotation.

When a uniform magnetic field is applied, there is a tendency for the field to align the net orbital angular momentum which is thus partially unquenched. The result is a paramagnetic contribution to the susceptibility. This partial unquenching is of such a nature that the average value of the component of orbital angular momentum in the direction of the field is no longer zero. Superimposed upon this unquenched orbital angular momentum is, of course, the usual Larmor precession which opposes it and which gives a diamagnetic effect. Whether a molecule is diamagnetic or paramagnetic depends upon which effect dominates. A molecule which is likely to be paramagnetic is thus seen to be a system (1) which possesses a large quantity of (quenched) orbital angular momentum in the absence of the field and (2) whose orbital angular momentum is unquenched to a large degree by a magnetic field. The amount of orbital angular momentum of a molecule is intimately related to the nodal structure of its wavefunction, thus relating the physical explanation of closed-shell paramagnetism to the mathematical discussion given in the earlier sections. The degree of unquenching, on the other hand, depends primarily upon the spectral energy separations between the ground and excited electronic states of the molecule, being greater when low-lying excited states are present. A paramagnetic molecule is also likely to exhibit the phenomenon of magnetic antishielding, resulting in a low-field chemical shift, since the unquenched electronic orbital angular momentum is likely to create a magnetic field at the nucleus which is in the same direction as the applied external field.

We also remark that the concept of negative "slippage" becomes less mysterious within this framework since slippage is shown to be related simply to unquenching of orbital angular momentum by the magnetic field due to molecular rotation.

We conclude by restating that the explanation for weak temperature-independent paramagnetism is possible within the Van Vleck theory of magnetic susceptibilities. We also emphasize, however, that although experimental evidence for weak paramagnetism exists, no *ab initio* numerical calculations have been performed upon systems for which experimental data are available. On the other hand, an *ab initio* coupled Hartree–Fock treatment of the $^1\Sigma$ BH molecule predicts this molecule to be paramagnetic,[26] but (1) there is no experimental value for the susceptibility of the BH molecule with which to compare this result, and (2) the Hartree–Fock perturbation theory used in this calculation is only an approximation to the Van Vleck formulation, although calculations on other molecules suggest it may be a rather good one.[27] An experimental determination of the susceptibility or of the rotational g factor of the BH molecule is therefore highly desirable. A quantitative agreement between theory and experiment for BH, for example, would be the first conclusive verification of the theory of temperature-independent paramagnetism.

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[26] R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. **42**, 3666 (1965); R. A. Hegstrom and W. N. Lipscomb, *ibid.* **45**, 2378 (1966). Further calculations employing a more accurate configuration-interaction wave function give similar results. [R. A. Hegstrom and W. N. Lipscomb (unpublished work)].

[27] W. N. Lipscomb in *Advances in Nuclear Magnetic Resonance*, J. T. Waugh, Ed. (Academic Press Inc., New York, 1966), Vol. 2 and references therein.