[23] However, it can also be found with the aid of the pertinent expansion coefficients Eq. (15) and the orthogonality relation Eq. (A9).

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[25] Another interpretation with the aid of Eq. (31) is also known. In the core of the line, the optical depth is such that the contribution by the layers near the boundary to the emitted radiation is dominant. The local excitation temperature defined there in the usual way by $n(2)/n(1)$ is low. Therefore, the radiation temperature at this frequency is low as well. Proceeding along the frequency scale to the wings, the optical depth decreases and more layers with a higher excitation temperature contribute. Hence, the radiation temperature at these frequencies increases. For frequencies defined by $k(u)L/\cos\alpha \leq 1$, the slab is optically thin. All layers are now equivalent. The decrease in the intensity of the radiation follows the common Doppler profile, as already proved in Eq. (33).

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Appraisal of an Iterative Method for Bound States*

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An iterative method for determining bound-state eigenvalues and properties of the radial Schrödinger equation is appraised. The method stems from iterating the integral equation $\psi = \mu(T + \frac{1}{2}\gamma^2)^{-1}(-V\psi)$, where T and V are the kinetic- and potential-energy operators. The basic theory is briefly reviewed, and calculations are performed for the Coulomb and screened-Coulomb potentials. The lowest three μ eigenvalues, together with the expected values of $(\gamma r)^{-1}$, γr, and $(\gamma r)^2$, are obtained from a single iterated eigenfunction sequence. Convergence is rapid for eigenvalues but slow for expected values. There is some sensitivity to the choice of the numerical integration formula. Regarded as a numerical method, this approach may be most competitive for the determination of zero-energy potential-strength eigenvalues. Its disadvantages are listed. Analytical improvements to eigenfunctions can be easier to obtain by iteration than by perturbation, and some success has been achieved. A simple example suggests that the rate of convergence of an iterated eigenfunction sequence is less than that of a related perturbation sequence unless the choice of starting function is bad.

I. INTRODUCTION

In this paper, we report on the utility of an iterative method for calculating bound-state eigenvalues and properties associated with the radial Schrödinger equation

$$(T+\mu V)\psi = -\tfrac{1}{2}\gamma^2\psi, \qquad \gamma \geqslant 0 \tag{1}$$

$$\text{where} \quad T(r) = -\tfrac{1}{2}\frac{d^2}{dr^2}, \quad 0 \leqslant r < \infty \tag{2}$$

is the kinetic-energy operator, $V(r)$ is the potential energy, and $\psi(r)$ is the *r-multiplied* radial wave function. The method is based on an integral-equation equivalent of (1), namely,

$$\psi = \mu(T+\tfrac{1}{2}\gamma^2)^{-1}(-V\psi), \tag{3}$$

which is formulated using the bound-state free-particle Green's operator $(T+\frac{1}{2}\gamma^2)^{-1}$ with kernel

$$\gamma^{-1}\{\exp(-\gamma|r-r'|)-\exp[-\gamma(r+r')]\}. \tag{4}$$

The alternative form (3) of the Schrödinger equation has been called the conjugate eigenvalue equation. When γ is regarded as a fixed parameter, Eq. (3) gives rise naturally to eigenvalues and eigenfunctions for the potential strength μ; often (most simply by scaling procedures) it is possible to relate them to energy eigenvalues and eigenfunctions for a prescribed μ.[1]

We employ the iterative sequence $\{\phi_k\}$ specified by

$$\phi_{k+1} = (T+\tfrac{1}{2}\gamma^2)^{-1}(-V\phi_k), \quad k=0,1,2,\ldots, \tag{5}$$

which ultimately behaves like a constant times the eigenfunction ψ_0 of (3) which corresponds to $\mu_0(\gamma)$, the μ eigenvalue of smallest magnitude. Illustrative numerical calculations are performed for the Coulomb potential, and also for the screened-Coulomb potential. Properties of the lowest three eigenstates are obtained from a single iterative sequence. The convergence of expected values is slow but steady, and the convergence of bounding sequences for eigenvalues is rapid.

Regarded as a numerical technique, the iterative method is akin to the power method for finding the eigenvalues of a matrix. It is likely to be competitive only for the lowest eigenstates, and most competitive for zero-energy states where more sophisticated methods[2,3] might run into difficulties because of their dependence on the adjustment of γ.

As an analytical method of improving approximate wave functions and estimating eigenvalues, this iterative approach has enjoyed success from time to time. Activity has been mainly in momentum space where an integral equation arises naturally as the Fourier transform of the Schrödinger equation.[4-9] But there has been some work in coordinate space[10,11] and recently considerable attention has been paid to eigenvalue bounds derived from the conjugate eigenvalue equation.[12-16] The present paper is concluded with a simple example which suggests that the rate of convergence of the sequence $\{\phi_k\}$ is less than that of a related perturbation sequence unless the choice of ϕ_0 is a bad one. However, analytical improvements to wave functions are, in principle, easier to obtain by iteration than by perturbation.

II. GENERAL THEORY

The theory is clear-cut when the operator $(-V)$ is positive definite, thus admitting a square root, and given that the operator

$$K = (-V)^{1/2}(T+\tfrac{1}{2}\gamma^2)^{-1}(-V)^{1/2} \tag{6}$$

is a Hilbert-Schmidt operator (i.e., K has finite double norm). Equation (3) may then be written

$$\{(-V)^{1/2}\psi\} = \mu K\{(-V)^{1/2}\psi\}, \tag{7}$$

and the standard Hilbert-Schmidt theory of integral equations invoked.[17,18] The potential strength μ has a discrete spectrum $\{\mu_n\}$ whose members can be arranged in ascending order of magnitude

$$0<\mu_0<\mu_1<\cdots<\mu_n<\cdots. \tag{8}$$

(In general, there could be some equalities here, but not for a one-dimensional radial problem.) If $\{\psi_n\}$ are the corresponding eigenfunctions, orthonormalized so that

$$(\psi_n, (-V)\psi_m) = \int_0^\infty \psi_n(-V)\psi_m\, dr = \delta_{nm}, \tag{9}$$

then it follows from the Hilbert-Schmidt theorem that

$$\phi_k = \sum_{n=0}^{\infty} a_n \mu_n^{-k}\psi_n, \qquad k=1,2\ldots, \tag{10}$$

where $a_n = (\phi_0, (-V)\psi_n)$, (11)

and the initial function ϕ_0 need not necessarily be in the domain spanned by $\{\psi_n\}$. Assuming that a_0 is not zero, the sequence $\{\phi_k\}$ ultimately behaves like a constant times ψ_0, and (if a_1 is also nonzero) the rate of convergence is governed by the ratio μ_0/μ_1. Thus, if $\mathfrak{L}(r)$ is an operator of interest and

$$L_k = (\phi_k, \mathfrak{L}\phi_k)/(\phi_k, \phi_k)\,, \tag{12}$$

the sequence $\{L_k\}$ will tend to the expected value of $\mathfrak{L}(r)$ in the bound state which is specified by the parameter values μ_0 and γ.

It can also be shown that[19]

$$A_0 \geqslant B_0 \geqslant A_1 \geqslant B_1 \cdots \geqslant A_k \geqslant B_k \cdots \geqslant \mu_0\,, \tag{13}$$

where $A_k = v_{kk}/v_{k,k+1}\,,\quad B_k = v_{k,\,k+1}/v_{k+1,k+1}\,,$ (14)

and $v_{ij} = \int_0^\infty \phi_r(-V)\phi_j\,dr\,.$ (15)

The sequences $\{A_k\}$ and $\{B_k\}$ actually have limit point μ_0, and their rate of convergence is governed by the ratio (μ_0/μ_1).

If a_0 (but not a_1) happens to be zero, then ϕ_k tends to a constant times ψ_1, and we obtain bounding sequences for μ_1. If μ_0 is known, then the sequence $\{\tilde{\phi}_k\}$ defined by

$$\tilde{\phi}_k = \mu_0\phi_{k+1} - \phi_k \tag{16}$$

always has a zero $\tilde{a}_0$, since

$$\tilde{a}_0 = (\tilde{\phi}_0, (-V)\psi_0) = (\mu_0\phi_1, (-V)\psi_0) - (\phi_0, (-V)\psi_0)\,, \tag{17}$$

and from Eqs. (3) for ψ_0 and (5) with $k=0$ the terms on the right-hand side of (17) are seen to cancel. Similarly, if

$$\tilde{\tilde{\phi}}_k = \mu_1\tilde{\phi}_{k+1} - \tilde{\phi}_k\,, \tag{18}$$

then $\tilde{\tilde{a}}_0$ and $\tilde{\tilde{a}}_1$ are zero and $\tilde{\tilde{\phi}}_k$ tends to a constant times ψ_2, and so on. These ideas were first developed and applied to vibration problems by Temple[20-22] and Bickley.[22] In the event that the powers of the dominant eigenvalue make ϕ_k too small as k increases (so that accuracy is lost), powers of an appropriate scale factor can be introduced. We can work with $\phi_k P^{-k}$, $\tilde{\phi}_k Q^{-k}$, etc., when P, Q are very rough estimates of μ_0, μ_1, etc.

Certain relaxations of the Hilbert-Schmidt condition on K are possible[23]; as far as μ_0 and ψ_0 are concerned, the method is not likely to be affected by the presence of a continuum at the upper end of the μ spectrum. If the operator $(-V)$ is indefinite, Eq. (3) must be treated in the form

$$(-V)\psi = \mu\,\{(-V)(T + \tfrac{1}{2}\gamma^2)^{-1}(-V)\}\psi\,. \tag{19}$$

The operator on the right-hand side of (19) is positive definite and self-adjoint, but the signs of the eigenvalues are now uncertain and negative eigenvalues may well not be physically relevant. The inequalities (8) and (12) are replaced by[19]

$$0 < |\mu_0| \leqslant |\mu_1| \leqslant \cdots \leqslant |\mu_n| \leqslant \cdots\,, \tag{20}$$

and $|B_0| \geqslant |B_1| \geqslant \cdots \geqslant |B_k| \geqslant \cdots \geqslant |\mu_0|\,.$ (21)

Nothing can be said here about the sequence $\{|A_k|\}$.

Whenever for a given value of μ the quantity $-\frac{1}{2}\gamma^2$ is a discrete energy which is not embedded in a continuum, physical considerations indicate that the entire μ spectrum is discrete for that value of γ.

III. SCREENED COULOMB POTENTIAL

The negative screened-Coulomb potential has been studied in connection with the deuteron,[7-9] hydrogen plasmas,[24] scattering theories,[25] and has recently been the subject of a perturbation treatment.[26] Let

$$V(r) = -r^{-1}e^{-\beta r}\,,\quad \beta \geqslant 0\,. \tag{22}$$

Then the double norm of K is, from (4), (6), and (22),

$$I(\beta,\gamma) = \gamma^{-2}\int_0^\infty\int_0^\infty (rr')^{-1}\exp[-\beta(r+r')] \times\{\exp[-\gamma\,|r-r'|\,] - \exp[-\gamma(r+r')]\}^2\,dr\,dr'\,, \tag{23}$$

which satisfies the relations

$$0 < I(\beta,\gamma) < I(0,\gamma) = \pi^2/\gamma^2\,, \tag{24}$$

$$I(\beta, 0) = 4\beta^{-2}\ln(4/e)\,, \tag{25}$$

and is thus finite unless both β and γ are zero. Hence, K is Hilbert-Schmidt.

Remembering that $\psi(r)$ is r multiplied, we set

$$\phi_k = r\theta_k\,, \quad k = 0, 1, 2, \ldots, \tag{26}$$

so that Eq. (5) becomes

$$r\theta_{k+1}(r) = \gamma^{-1}\int_{r'=0}^{\infty}\{\exp[-\gamma\,|r-r'|\,] - \exp[-\gamma\,(r+r')]\}\times\exp(-\beta r')\,\theta_k(r')\,dr', \tag{27}$$

which reduces to

$$\theta_{k+1}(0) = 2\int_{r'=0}^{\infty}\exp[-(\beta+\gamma)r']\,\theta_k(r')dr' \tag{28}$$

at zero r. If γ is zero (corresponding to zero-energy bound states), Eq. (27) simplifies to

$$r\theta_{k+1}(r) = 2\int_{r'=0}^{\infty}\min\{r, r'\}\,e^{-\beta r'}\,\theta_k(r')\,dr'\,. \tag{29}$$

Whenever suitable, Eqs. (27) and (28) can be recast in terms of a variable (γr); likewise Eq. (29) in terms of (βr).

IV. NUMERICAL RESULTS

Illustrative calculations of iterative sequences for eigenvalues (μ_n/γ) and expected values of $(\gamma r)^{-1}$, γr, and $(\gamma r)^2$ were performed for the Coulomb potential (Table I) and also for the screened-Coulomb potential with $\gamma = 0.313\beta$ (Table II). This particular ratio was used by Salpeter and Goldstein[8] for a deuteron model; they found an estimated value of 3.797 for (μ_0/γ) in comparison with our 3.91770. In Table III appear the eigenvalue sequences for the zero-energy screened-Coulomb potential. Here our values of $(2\mu_n/\beta)$ for the lowest three states are 1.683 74, 6.5066, and about 14.6. Harris[24] has obtained approximate values 1.74, 7.14, and 13.33 by a variational method, and the directly calculated value for $(2\mu_0/\beta)$ of 1.683 by Sachs and Goeppert-Mayer[27] is still quoted in the more recent literature.[25,28] (Expected values of powers of r are not relevant for this latter system.)

TABLE I. Hydrogenic states: $\beta = 0$.

	k	$(\mu_n/\gamma)_+$	$\langle(\gamma r)^{-1}\rangle$	$\langle\gamma r\rangle$	$\langle(\gamma r)^2\rangle$
$n=0$	2	1.020 58	1.218 45	1.233 36	2.042 25
	5	1.000 31	1.021 74	1.463 95	2.859 34
	8	1.000 00	0.999 78	1.495 38	2.981 62
	11	1.000 00	0.997 07	1.499 43	2.997 69
	16	1.000 00	0.996 69	1.499 99	2.999 95
	Exact	1	1	1.5	3
$n=1$	2	2.048 56	0.659 04	2.510 28	7.508 55
	5	2.004 18	0.539 68	2.849 26	9.524 12
	8	2.000 36	0.510 11	2.954 26	10.200 61
	11	2.000 03	0.501 79	2.986 30	10.413 03
	16	2.000 00	0.498 77	2.998 21	10.492 87
	Exact	2	0.5	3	10.5
$n=2$	2	3.086 72	0.479 10	3.699 47	16.222 5
	5	3.015 31	0.384 79	4.158 40	19.955 9
	8	3.002 68	0.352 86	4.354 33	21.677 1
	11	3.000 79	0.340 32	4.439 27	22.446 6
	Exact	3	0.333 33	4.5	23
$n=3$	2	4.134 43	0.392 05	4.802 76	27.637 8
	5	4.035 04	0.308 27	5.403 71	33.755 8
	8	4.002 14	0.272 94	5.727 26	37.258 6
	Exact	4	0.25	6	40.5

TABLE II. Screened Coulomb potential: $\gamma = 0.313\beta$.

	k	$(\mu_n/\gamma)_+$	$\langle(\gamma r)^{-1}\rangle$	$\langle\gamma r\rangle$	$\langle(\gamma r)^2\rangle$
$n=0$	2	3.960 21	2.096 77	0.782 33	0.904 07
	5	3.917 71	2.315 56	0.734 04	0.820 38
	8	3.917 70	2.319 73	0.733 28	0.819 16
	11	3.917 70	2.319 82	0.733 27	0.819 13
	16	3.917 70	2.319 82	0.733 27	0.819 13
$n=1$	2	14.931 9	1.238 22	1.080 14	1.478 62
	5	14.157 8	1.477 90	0.974 06	1.249 66
	8	14.153 8	1.496 32	0.968 07	1.237 84
	11	14.153 8	1.497 68	0.967 61	1.236 94
$n=2$	2	37.367	0.929 69	1.306 28	2.027 70
	4	33.497	1.102 95	1.176 06	1.699 53
	6	33.281	1.152 82	1.149 50	1.639 02
	7	33.266	1.162 13	1.145 24	1.629 63
$n=3$	2	78.8	0.773	1.492	2.550
	4	66.7	0.909	1.344	2.132
	6	63.4	0.944	1.308	2.036

A typical iteration integral like (27) was replaced by the discrete approximation

$$x_i\theta_{k+1}(x_i/\gamma) = \textstyle\sum_j\{\exp[-\,|x_i - x_j\,|\,] - \exp[-(x_i + x_j)]\}\times\exp(-\beta x_j/\gamma)\theta_k(x_j/\gamma)\,\omega_j\,, \tag{30}$$

where $x = \gamma r$ and (x_j, ω_j) are the points and weights of the numerical-integration formula. The same integration formula was used to evaluate all the integrals in a single program, thus saving a factor of about 100 in time. The particular formula used to give the results in Tables I-III was a trapezoidal rule with 100 equal intervals from 0.0 to 10.0, combined with a 19-point Gauss-Laguerre quadrature formula from 10.0 to ∞. The trapezoidal rule was chosen because the discontinuity in the slope of the kernels should have no effect on it. Beyond $x = 10.0$ there is little contribution to the integral and different means used to integrate the tail of the integrand gave similar results. In each case the starting function was $\theta_0 = e^{-3x/2}$, but the iteration is insensitive to choice of starting function. After one or two cycles, similar results were obtained with, for example, $\theta_0 = 1$.

Sixteen iterations were performed, and the bounding sequences $\{A_k\}$ and $\{B_k\}$ given by (14) were stable through eight figures after twelve iterations.

Only the sequence $\{B_k\}$ is quoted in the tables [designated by $(\mu_n/\gamma)_+$ and $(2\mu_n/\beta)_+$] since $A_k \geqslant B_k$, and only some of the k values are shown to save space. Appropriate $\{L_k\}$ sequences are also given. Only a single sequence $\{\theta_k\}$ was calculated for each of the three systems, and sequences suitable for the next highest states were deduced from it, as indicated in Eqs. (16) and (18). Although this method of finding subdominant eigenvalues is highly subject to round-off errors, the calculations were stable through 16, 11, and 8 iterations for the next three hydrogenic states, and through rather fewer iterations for the other systems (the highest k value shown is the last stable one for $n = 1, 2, 3$). Better accuracy could, of course, be obtained for $n > 0$ if a fresh iterative sequence were generated for each state, with renormalization at appropriate stages. But such refinements consume more machine time, and were felt to be unjustified in the present context. The calculations were run in FORTRAN on a CDC 3600 computer in single-precision arithmetic which is good to about 10 significant figures, and the average running time including compilation was about 40 sec.

In an attempt to improve the expected value of $(\gamma r)^{-1}$ for hydrogen (which for $n = 0$ is 0.3% too low), an alternative integration formula was tried with 40 equal intervals in 0.0 to 2.0, 80 intervals in 2.0 to 10.0, and the same 19-point Gauss-Laguerre formula past 10.0. The main effect of this change was to lower the eigenvalue results in about the fourth significant figure, but the $(\gamma r)^{-1}$ values were improved slightly. This fact, combined with the stable convergence of the eigenvalue sequence with each formula, would seem to indicate that the iterative method is somewhat sensitive to the particular integration formula in use. Because of the excellent results for the first two hydrogenic eigenvalues, we put our faith in the trapezoidal rule with equal intervals from 0.0 to 10.0.

V. COMPARISON WITH PERTURBATION THEORY

As a simple example let us consider the hydrogenic ground state where $\mu_0 = 1$, $\gamma = 1$, and $\psi_0 = re^{-r}$ (not normalized). The overlap of $\phi_k\,(= r\theta_k)$ with $r\exp(-r)$ is

$$S_k = \int_0^\infty \theta_k(r) e^{-r}\, r^2\, dr . \tag{31}$$

If we also define

$$C_k = \int_0^\infty \theta_k(r)\, \exp(-r) r\, dr\ , \tag{32}$$

then it follows from (27) with $\beta = 0$, $\gamma = 1$ that

$$C_k = C_0, \quad \text{(independently of } k) \tag{33}$$

$$\text{and} \quad S_k = C_0 + (S_0 - C_0)2^{-k} \quad . \tag{34}$$

The rate of convergence of the overlap integral S_k is thus exactly $\frac{1}{2}$ (the value of μ_0/μ_1) and this is independent of the initial trial function θ_0.

If we take

$$\chi_0 = \exp(-\alpha r), \quad \alpha \neq 1 \tag{35}$$

as the unperturbed wave function for a Rayleigh-Schrödinger perturbation expansion, the perturbation is $(\alpha - 1)/r$ and it is possible by standard methods[29] to determine χ_k, the wave function corrected through order k in the perturbation. For comparison with θ_k, the normalization is arranged so that

$$C_k' = \int_0^\infty \chi_k\, \exp(-r)\, r\, dr = C_0$$

$$\text{(independently of } k), \tag{36}$$

and the consequent overlap integral

$$S_k' = \int_0^\infty \chi_k\, e^{-r}\, r^2\, dr \tag{37}$$

has the value

$$S_k' = C_0 - C_0 \left(\frac{\alpha - 1}{\alpha + 1}\right)^{k+1} \quad . \tag{38}$$

Thus judging by the overlap integrals S_k and S_k', the perturbation approach to the true eigenfunction converges more rapidly than does the iterative approach whenever

$$[(\alpha - 1)/(\alpha + 1)] < \tfrac{1}{2}, \quad \text{i.e.,}\ \alpha < 3 \quad . \tag{39}$$

Since $\alpha = 1$ gives the true eigenfunction, the iterative approach is only superior when a bad initial trial function is chosen.

Qualitatively, one might expect a perturbation treatment to be better; ideally such a treatment

TABLE III. Screened-Coulomb eigenvalues at zero energy: $\gamma = 0$.

k	$(2\mu_0/\beta)_+$	$(2\mu_1/\beta)_+$	$(2\mu_2/\beta)_+$	$(2\mu_3/\beta)_+$
2	1.754 93	6.630 9	15.333 4	28.698
4	1.684 06	6.511 2	14.698 9	28.609
6	1.683 74	6.506 8	14.642 0	26.424
7	1.683 74	6.506 6	14.623 5	⋯
8	1.683 74	6.506 6	⋯	⋯
16	1.683 74	⋯	⋯	⋯

involves corrections resulting from a small perturbation to the potential, whereas in the iterative approach corrections are generated by the operator $(T+\frac{1}{2}\gamma^2)^{-1}(-V)$, involving the whole potential. However, the single quadrature required for an iterative correction to a wave function is in principle easier to carry out analytically than the double quadrature required for a first-order perturbed wave function.[29] Thus in some cases it may be possible to improve a wave function analytically by iteration but not by perturbation. It has been pointed out[10] that the first iterated improvement to a hydrogenic 1*s* function is a so-called 0*s* function.

VI. CONCLUDING REMARKS

As a numerical tool, this iterative method is conceptually very simple but it has shortcomings. These are (i) the difficulties with the basic theory if K is not Hilbert-Schmidt, (ii) the slow convergence of expected-value sequences, (iii) the difficulties in dealing with subdominant eigenvalues, (iv) the sensitivity of results to integration formulas, and (v) the possible difficulties in relating the two different types of eigenvalue equations. Perhaps these help to explain its relative lack of popularity. The method may well be seen to best advantage in the calculation of zero-energy potential-strength eigenvalues, which are useful in determining the number of bound states admitted by a given potential.[1]

As an analytical method, the approach has enjoyed some success devolving from its simple Green's operator. It may be useful occasionally when perturbation theory fails.

Equation (1) which we considered was for *s* states. For states with higher-orbital angular momentum, one can either work with the operator

$$\{T+2i(l+1)r^{-2}+\tfrac{1}{2}\gamma^2\}^{-1} \tag{40}$$

which has kernel

$$2(rr')\,I_{l+1/2}(\gamma r_<)\,K_{l+1/2}(\gamma r_>)\,,$$
$$(r_< = \min[r,r'],\quad r_> = \max[r,r'])\,, \tag{41}$$

where $I_{l+1/2}$ and $K_{l+1/2}$ are the modified spherical Bessel functions, or alternatively the r^{-2} term might be absorbed into the potential.

If the Schrödinger equation is many-dimensional and nonseparable the difficulties mount. But some analytical progress has been made for He and H_2^+,[5, 6, 15] and the numerical approach may well be feasible, certainly in two dimensions. The free-particle Green's function in n dimensions is known.[30]

Methods which combine features of the two types of eigenvalue equations (1) and (3) have been suggested.[11, 31]

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Possibility of Field-Dependent Nuclear Magnetic Shielding

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The possibility of an observable field dependence of the nuclear magnetic shielding in NMR experiments is discussed. It is shown that in most molecules such an effect should be unobservably small. However, in some molecules, especially where the magnetic shielding is abnormally large, it is possible that the field dependence of the shielding could be large enough to be observable. In NMR experiments of high accuracy in strong magnetic fields, the proportionality of the resonance frequency to the magnetic field should therefore not be automatically assumed, but should be experimentally verified.

I. INTRODUCTION

When a single nuclear magnetic resonance line is observed with liquids, it is generally presumed that the resonance frequency is exactly proportional to the external magnetic field. This presumption has indeed been supported by those past experiments in which the proportionality has been tested. However, in many of the highest-resolution NMR experiments on chemical shifts, a small field dependence of the magnetic shielding would escape notice since the resonances are often measured at only a single magnetic field. It is the purpose of this paper to point out that as nuclear resonance experiments are performed with greater precision and in higher magnetic fields, there is reason in some cases to expect small departures from exact proportionality between the resonance frequency and the magnitude of the external magnetic field H_0.

II. FIELD-DEPENDENT NUCLEAR MAGNETIC SHIELDING

Departures from simple proportionality between the resonance frequency and the field can arise from a magnetic field dependence of the nuclear magnetic shielding.[1] Thus, if σ^T represents the total magnetic shielding and if σ is the usual field-independent shielding, the total shielding should be field-dependent and given by

$$\sigma^T = \sigma + \tau H_0^2 + \cdots , \tag{1}$$

where τ is a molecular coefficient defined by the above relation. The odd powers of H_0 in Eq. (1) vanish by the symmetry requirement that the magnitude of the shielding must be independent of the direction of the magnetic field. The term in H_0^2 in Eq. (1) will give rise to a cubic dependence of the angular resonance frequency ω upon H_0 since

$$\omega = (1-\sigma^T)\gamma H_0 = (1-\sigma)\gamma H_0 - \tau\gamma H_0^3 \ . \tag{2}$$

It should be noted that although the value of σ can not be empirically obtained by observations of the dependence of ω upon H_0, the value of τ can be found in this manner.

Quadratic terms in the magnetic shielding would be expected both from higher-order perturbation shifts of the energy levels of specific molecular states and from slight shifts in the distribution of population among the different states upon application of the magnetic field. As discussed previously,[1] the perturbation with the external field H_0 and the relevant magnetic moment μ taken parallel to the z axis is given by

$$\mathcal{H}^{(1)} + \mathcal{H}^{(2)} = -\textstyle\sum_k (H_0 + 2\mu/r_k^3) m_{zk}^0 + (e^2/8mc^2)\textstyle\sum_k (H_0 + 2\mu/r_k^3)^2 (x_k^2 + y_k^2) \ , \tag{3}$$

where m_{zk}^0 is the z-component orbital magnetic moment operator.[1] With this, the fourth-order perturbation calculation of the energy can be carried out in the usual manner.[2] If W_λ'' represents