

# THE JOURNAL OF PHYSICAL CHEMISTRY

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VOLUME 84, NUMBER 22 OCTOBER 30, 1980

## LETTERS

### Efficient Computation of Magnetic Resonance Spectra and Related Correlation Functions from Stochastic Liouville Equations

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It is found that a very powerful method for computing slow-motional ESR (and NMR) spectra may be developed by the use of the Lanczos algorithm (LA) modified to tridiagonalize complex-symmetric matrices. It leads to *at least* order of magnitude reductions in computation time and in computer storage requirements than the commonly used Rutishauser algorithm. This permits the rapid analysis of spectral problems that were previously too difficult. The formal similarity of these problems to those from Fokker-Planck equations in molecular dynamics suggests that the LA should also be a very powerful method for the latter.

In recent years there has been extensive work demonstrating that slow-motional studies of ESR (and NMR) can, when properly analyzed, provide detailed information on the microscopics of molecular motions in condensed phases.<sup>1</sup> The extent of resolution and interpretation of such spectra has reached the degree that simple models (e.g., Brownian diffusion or jump models) no longer are necessarily adequate.<sup>2-4</sup> This poses two problems in such research. The first is the increasing complexity of the expressions (derived from the stochastic Liouville equation [SLE]) that are needed to interpret the spectra. The second is the construction of reasonably realistic microscopic models for the molecular dynamics. We have recently addressed ourselves to the latter by developing augmented stochastic Liouville (or Fokker-Planck) expressions consistent with the physics of the relevant molecular motions, the coupling to bath variables, and the constraints of detailed balance with respect to a (quasi-) equilibrium state.<sup>2,5</sup> However, such stochastic modeling quickly leads to augmented SLE in several variables that

are increasingly difficult to solve. Thus we are again lead back to the first problem. In this letter we wish to communicate what we have found to be a very powerful method for dealing with the problem. We particularize our discussion to the line-shape analysis for convenience, but we note that the calculation of correlation functions from Fokker-Planck forms will be very similar.

The stochastic-Liouville equation may be expressed in the form<sup>6</sup>

$$\partial \rho(\Omega) / \partial t = -i\mathcal{H}(\Omega) \times \rho - \Gamma_{\Omega} \rho(\Omega, t) \quad (1)$$

where  $\mathcal{H}(\Omega)$  is the spin Hamiltonian, and we use the superoperator notation  $A \times B \equiv [A, B]$ , while  $\Omega$  represents the set of dynamical molecular variables of the spin-bearing molecule,  $\Gamma_{\Omega}$  is the Markovian Fokker-Planck operator in the set of variables  $\Omega$ , and  $\rho(\Omega)$  is the spin-density matrix which is also a classical probability function in  $\Omega$ . We associate with  $\Gamma_{\Omega}$  the unique "equilibrium"  $P_0(\Omega)$  such that  $\Gamma_{\Omega} P_0(\Omega) = 0$ . The spectrum is computed by taking the Fourier-Laplace transform of the trace of  $S_x$ , the spin

operator, with  $\rho(\Omega, t)$  subject to an initial condition (or else an "instantaneous equilibrium distribution") which is given by a vector  $|v\rangle$  (the "right-hand vector") defined in the "Liouville" space, which is a product of spin space and the Hilbert space of the variables  $\Omega$  (for which a convenient basis set is used). This leads to a form for the unsaturated spectrum that we may write as<sup>1,6,7</sup>

$$I(\omega) = \frac{1}{\pi} \text{Re} \{ \langle v | [i(\omega 1 - \mathcal{H}(\Omega)^x) + \tilde{\Gamma}_\Omega]^{-1} | v \rangle \} \quad (2)$$

where  $\langle v |$  and  $|v\rangle$  are bra and ket vectors in the space defined by  $\mathbf{A} \equiv -i\mathcal{H}(\Omega)^x + \tilde{\Gamma}_\Omega$  with  $\tilde{\Gamma}_\Omega \equiv P_o(\Omega)^{-1/2} \Gamma_\Omega P_o(\Omega)^{1/2}$  which may generally be written as a (complex) symmetric matrix while  $\mathcal{H}(\Omega)^x$  is Hermitian and can generally be written as a real symmetric matrix. Also  $|v\rangle = P_o(\Omega)^{-1/2} |v'\rangle$  while  $\langle v |$  is just the transpose of  $|v'\rangle$ . Thus, scalar products (e.g.,  $\langle v | v \rangle$ ) are defined without regard to the complex number properties of the vectors. [Alternatively, spectral densities (i.e., the Fourier-Laplace transforms of correlation functions) from Fokker-Planck equations can be calculated from the expression formally identical with eq 2 but with  $\mathcal{H}(\Omega)^x = 0$  and with the real parts of  $\Gamma_\Omega$  representing irreversible drift and diffusive terms while the imaginary part of  $\Gamma_\Omega$  represents reversible drift terms.]<sup>5</sup>

While  $I(\omega)$  may be obtained by inversion methods, diagonalization is usually preferred since the former must be repeated for each value of  $\omega$ .<sup>8,9</sup> Thus, we may write

$$\mathbf{A}\mathbf{X} = \Lambda\mathbf{X} \quad (3)$$

as the eigenvalue problem with the eigenvectors determining a (complex) orthogonal transformation  $\mathbf{X}$ , and  $(\Lambda)_{mn} = \lambda_m \delta_{mn}$ . We let

$$|u\rangle = \mathbf{X}^u |v\rangle \quad (4)$$

so that

$$I(\omega) = \frac{1}{\pi} \text{Re} \{ \langle u | (i\omega 1 + \Lambda)^{-1} | u \rangle \} = \frac{1}{\pi} \text{Re} \sum_m \frac{u_m^2}{i\omega + \lambda_m} \quad (5)$$

Equation 5 has in the past been typically solved by means of an algorithm originally introduced by Rutishauser<sup>1,8,10</sup> that reduces a symmetric (complex) matrix to tridiagonal form, while preserving the banded form at all stages. We hereafter refer to it as the Rutishauser algorithm (RA).

We recently developed a form of this algorithm that is optimized for use on limited-core minicomputers with disk access. Our version (1) maximizes the number of matrix elements (of the extradiagonal) that are reduced to zero (by Jacobi rotations) in each passage through the matrix and (2) maximizes the efficiency of communication of matrix elements between disk and core.<sup>11</sup> The efficiency of operation of this version allowed us to develop programs to solve problems with even more degrees of freedom than had hitherto been programmed for the large core IBM 370/168; e.g., (a) in the problem of a nitroxide radical where the molecular axes of the magnetic tensor and the diffusion tensor do not coincide,<sup>12</sup> we could readily include a nonzero azimuthal *as well as* polar angle, while (b) for liquid crystalline programs, we could allow for arbitrary tilt of the director relative to the magnetic field. Case (2) had been a formidable<sup>13</sup> (but very important<sup>14</sup>) task, because cylindrical symmetry in the lab frame is destroyed. However, there are limits of time and core that prevent us from combining both (a) and (b) into a single program that runs on a minicomputer or on a large computer in affordable times.

We have now found that, by means of the Lanczos algorithm (LA)<sup>15</sup> (very closely related to the method of moments<sup>16,17</sup>), we are able to achieve, *at the least*, an order

of magnitude reduction in computational time as well as in computer storage requirements over previous programs based on the RA! The LA is an iterative procedure that generates a new basis set in which  $\mathbf{A}$  is tridiagonal. In the truncated Hilbert space of dimension  $N$  of the initial basis set, we consider that the first  $n$  elements of the new basis set  $|k\rangle$  for  $k = 1, \dots, n$  have been computed. Then  $|n+1\rangle$  is generated from  $|g\rangle \equiv \mathbf{A}|n\rangle$  by projecting out all but the part of  $|g\rangle$  orthogonal to the  $n$ -dimensional subspace defined by the  $|k\rangle$  for  $k = 1, \dots, n$ . One obtains as the basic relation<sup>15</sup>

$$\beta_n |n\rangle = (\mathbf{A} - \alpha_{n-1})|n-1\rangle - \beta_{n-1}|n-2\rangle \quad (6)$$

where  $\beta_n$  is the normalizing coefficient, so that  $\langle n | n \rangle = 1$  and is seen to be given by  $\beta_n = \langle n | \mathbf{A} | n-1 \rangle$ , while  $\alpha_n \equiv \langle n | \mathbf{A} | n \rangle$ . Equation 6 is a recursion relation such that  $|n\rangle$  is determined solely from  $|n-1\rangle$  and  $|n-2\rangle$ , the  $\alpha_{n-1}$ ,  $\beta_{n-1}$ , and the effect of operating on  $|n-1\rangle$  by  $\mathbf{A}$ . It clearly leads to tridiagonal form in the new basis with  $\alpha_n$  as diagonal elements and  $\beta_n$  as the superdiagonal elements. The most convenient starting vector  $|1\rangle$  is just  $|v\rangle$  as may be seen from eq 2 or eq 4 and 5.

With this algorithm, eq 2 may be shown to become

$$I(\omega) = \frac{1}{\pi} \text{Re} \langle 1 | [i\omega 1 + \mathbf{T}_n]^{-1} | 1 \rangle \quad (7)$$

where  $\mathbf{T}_n$  is the matrix representation of  $\mathbf{A}$  after  $n$  iterative steps in the new basis set. This tridiagonal matrix may now be diagonalized by the usual (QR transform) algorithm<sup>8,10b</sup> or else it may be computed by continued fractions,<sup>18</sup> which we find to be much faster. [The running time of the QR transform goes as  $n^2$  while the final summation over eigenvalues (eq 5) for each value of  $\omega$  goes as  $n$ ; the continued fraction solution is about as fast as just this latter step.] Our application of the LA to complex-symmetric (hence nonmetric) space is the first we are aware of, and for which the existing theorems are not rigorous but useful nevertheless.<sup>15,16,19a</sup>

The positive consequences of this algorithm are the following:

(1) Only the storage of the two vectors  $|n-1\rangle$  and  $|n-2\rangle$  is strictly required at any given time, since one may compute the matrix elements of  $\mathbf{A}$  as needed.

(2) The LA allows one to take into account (in both computation and storage) the sparseness of  $\mathbf{A}$ , since the LA *never modifies*  $\mathbf{A}$ , whereas the RA operates directly on and modifies  $\mathbf{A}$ , so its sparseness is lost.

(3) The iterative steps can be stopped before the end, i.e., for  $n < N$ , when the spectrum (calculated by continued fractions) has been found to have converged (with the  $\alpha_i$ ,  $\beta_i$  for  $i > n$  either truncated or else asymptotically approximated<sup>17,19a</sup>).

It is these three consequences that make the LA much more efficient than the RA.

However, the LA is not stable, whereas the RA is. Thus the negative consequences of this algorithm are the following:

(4) The vectors  $|n\rangle$  lose orthogonality as a result of round-off error; this effect becomes important when the number of iterative steps  $n$  is close to  $N$ .<sup>15b</sup> So, if it is not stopped, it could iterate ad infinitum.

(5) The LA cannot distinguish degenerate or even near-degenerate eigenvalues, but, instead, tends to generate a single eigenvector with a mean eigenvalue for such a "cluster" of the eigenvectors. [The origin of such a cluster is usually ambiguous because of effects of interaction among clusters.]

(6) The LA iterates so as to generate basis vectors  $|n\rangle$  associated with the highest eigenvalues in the problem, and

since typical forms of  $\Gamma_n$  are unbounded (i.e., their eigenvalue spectrum extends to infinity) the results could diverge.

Although we have found adequate manifestations of the weaknesses (4), (5), and (6), nevertheless, we do find that the LA yields excellent results for  $I(\omega)$  (when compared to the "rigorous" results of the RA) if only a few simple precautions are taken. Weakness (4) is more than compensated for by strength (3). In general, we find that one may stop at an  $n \ll N$  to obtain the excellent results for  $I(\omega)$ , because the additional steps do not contribute appreciably to the spectrum. That is, convergence to the correct  $I(\omega)$  is reached before round-off error can affect the results. Thus, we introduce the concept of the minimum optimal basis set (MOBS) of  $|n\rangle$ . Our experience has shown that the LA is very effective at approximately generating the smallest set of vectors, the MOBS, in which to represent  $I(\omega)$  in the tridiagonal form given by  $T_n$ . We find that (5), instead of being a weakness, is in practice a virtue in calculating  $I(\omega)$ , since we are not so much interested in the accurate eigenvalue spectrum as in the MOBS to represent  $I(\omega)$ . That is, the LA should be regarded as producing the basis set  $|k\rangle$ ,  $k = 1$  to  $n$ , that minimizes the error in  $I(\omega)$ , while it reduces the dimension of the space by having "clusters" represented by an eigenvector with a single mean eigenvalue and with a projection on  $|v\rangle$  that is the sum of that of the components as the "cluster". Finally, weakness (6) can be considerably reduced by truncating the initial basis set of dimension  $N$  such that it is as small as is consistent with accurate convergence, although the choice of  $N$  need not be very precise.

The efficiency of the LA with respect to computation time is directly related to (i) the ratio  $n/N$  where  $n$  is the number of steps required to accurately reproduce  $I(\omega)$ , and (ii) the sparseness of the matrix. The ratio of  $n/N$  varies from problem to problem, but typically decreases with increasing dimension of the matrix. A useful measure of the sparseness is the average number of matrix elements  $n_E$  different from zero for each row. This quantity depends on the nature of the ESR problem (e.g., the value of nuclear spin, symmetry of the magnetic and diffusion tensors), but it is almost independent of the dimension of the matrix. The parameter  $n_E$  determines the required storage space and the execution time for the LA in the same way that the bandwidth  $M$  affects the RA. Since  $n_E$  is always much less than  $M$  (in particular for nonaxial problems,  $M$  grows with the dimension of the matrix, while  $n_E$  remains constant), we find a large savings in computation time. Additionally, for large matrices, the computation time is further reduced in using the LA vs. the RA, because it is often possible to store the (nonzero) matrix elements in core memory for the LA, while the RA would require disk storage of the banded portion of the matrix (requiring much longer execution times for accessing disk-stored data).

As an indication of the power of the LA vs. the RA we note that a large nitroxide ESR spectral simulation (of type (a) or (b) above) requiring the  $N = 330$ , and with a running time of 6 h on a PDP 11/34 using the stable RA will, with the LA, accurately reproduce these results in 15 min! As the matrices increase in dimension even greater savings are to be anticipated. Furthermore, we note that, when utilizing the LA, the general features of the spectrum are obtained after only a few iterative steps; the later steps tend to fill in the details.<sup>19b</sup>

All these observations suggest that exceedingly difficult problems of large dimensions may be conveniently solved

by using the LA. Thus, for example, a computer program for ESR nitroxide simulation that combines both (a) and (b) (see above) yielding matrices of dimension  $N$  up to several thousand now appears feasible. It is a common problem in ESR studies on ordered phases of liquid crystals and of membrane systems.<sup>14,20</sup> In particular, from (1) we estimate that a matrix of  $N \sim 6000$  can be handled on a PDP 11 (e.g. 11/34 or 11/45) mincomputer (using a 140-Kbyte high-speed data memory and complex number double precision accuracy), while for a VAX computer configured with a 2-Mbyte core, the LA could be used for an  $A$  with  $N \sim 60000$ .<sup>21</sup> While at first, it would appear that such cases would be limited by time constraints, the possibilities (i) and (ii) (noted above) should significantly aid in reducing execution time.

The implications are that it should now be possible to rapidly and efficiently calculate ESR spectra in the slow-motional region for nearly all cases of practical interest<sup>22</sup> and utilizing sufficiently detailed descriptions of the molecular dynamics. Furthermore, the connection of the LA to the method of moments, for which extensive mathematical theory exists,<sup>16</sup> could be of considerable future value.

The details of our analysis of the LA algorithm applied to these problems will be given elsewhere.<sup>23</sup>

*Acknowledgment.* This work was supported by NSF Grants DMR-77-17510 and CHE77-26996.

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we believe, could make the LA a useful alternative to the methods of stochastic molecular dynamics (e.g., "Report on the Workshop-Stochastic Molecular Dynamics", D. Ceperley, Ed., NRCC, Berkeley, Calif., 1979).

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dimension possible, although with increased computation time.

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## The Proton Affinity of Ammonia. A Theoretical Determination

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The absolute proton affinity (PA) of ammonia has been calculated by using ab initio molecular orbital theory. Calculations at the SCF level were carried out with both Gaussian-type orbitals (GTO) and Slater-type orbitals (STO). The STO basis was used in CI calculations with all single and double excitations included. A correction for quadruple excitations was made. The zero-point energy difference between  $\text{NH}_3$  and  $\text{NH}_4^+$  was calculated at the SCF level with the GTO basis and appropriately scaled to experiment. The value calculated for  $\text{PA}(\text{NH}_3)$  is  $205.6 \pm 1$  kcal/mol.

### Introduction

Molecular proton affinities (PA) are important thermodynamic quantities related to the gas-phase basicity. A wide range of gas-phase proton affinities has been determined experimentally, especially through the use of ion cyclotron resonance (ICR) spectroscopy.<sup>1</sup> It is extremely difficult to measure absolute gas-phase proton affinities, since accurate heats of formation of ions must be known. Absolute proton affinities are, however, important quantities as they can be employed in various thermodynamic cycles to yield ion solvation energies. Most proton affinities have been measured as relative values with respect to certain standard molecules. The molecule whose proton affinity is typically used as a standard value is ammonia. The value for  $\text{PA}(\text{NH}_3)$  has been measured by a range of experimental techniques, from ICR to photoionization of van der Waals dimers generated in supersonic beams.<sup>1-5</sup> These experimental data are summarized in Table I.

As part of our combined experimental/theoretical studies of gas-phase ions,<sup>6</sup> we have been determining gas-phase proton affinities using ab initio molecular orbital theory. Since  $\text{NH}_3$  is a relatively simple molecule, we have focussed on an accurate calculation of its proton affinity.

Before describing the calculations and results in detail, we present a discussion of the quantities that must be determined in order to calculate a proton affinity for comparison with experiment. The proton affinity of a base B is generally defined experimentally as  $\text{PA}(\text{B}) = -\Delta H_{298}$  for reaction 1. From the ab initio calculations, we de-



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TABLE I: Experimental Proton Affinities (PA) of  $\text{NH}_3$

PA, kcal/mol	method	ref
202.3	ICR <sup>a</sup>	3
203.6	photoionization of $(\text{NH}_3)_2$	5
205.0	ICR <sup>a</sup>	1
$207 \pm 3$	high-pressure mass spectroscopy	4
$207.1 \pm 1.7$	ICR <sup>a,b</sup>	2
$208.5 \pm 1.5$	ICR <sup>a,c</sup>	2

<sup>a</sup> Ion cyclotron resonance spectroscopy. <sup>b</sup> Based on  $\text{PA}(i\text{-C}_4\text{H}_8)$  and  $\Delta H_f^\circ(\text{C}(\text{CH}_3)_3^+)$ . <sup>c</sup> Revision of data in ref 3.

termine a  $\Delta E$  quantity which is converted to a  $\Delta H$  as follows:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) \quad (2a)$$

$$\Delta H_{298} = \Delta E_{298} + \Delta nRT \quad (2b)$$

For reaction 1,  $\Delta n = -1$  in eq 2b. The quantity  $\Delta E$  can be described as a sum of  $\Delta E$  values which are dependent on the temperature:

$$\Delta E = \Delta E^{\text{elec}} + \Delta E^{\text{vib}} + \Delta E^{\text{rot}} + \Delta E^{\text{trans}} \quad (3)$$

The  $\Delta E^{\text{rot}}$  term is zero if we assume that  $\text{NH}_3$  and  $\text{NH}_4^+$  are classical rotors at 298 K while  $\Delta E^{\text{vib}}$  is negligible at 298 K. The term  $\Delta E^{\text{trans}}$  is simply  $-3/2RT$ . The  $\Delta E^{\text{elec}}$  term can be written as

$$\Delta E^{\text{elec}} = \Delta E_0^{\text{elec}} + \Delta E_{298}^{\text{elec}} + \Delta ZPE \quad (4)$$

where the middle term is negligible at 298 K. The first term is determined from the ab initio calculations while the last term is the difference in zero-point energies of  $\text{NH}_3$  and  $\text{NH}_4^+$ . This last term cannot be neglected, as an estimate from experimental values for the frequencies of