Fourier Grid Hamiltonian Method for Solving the Vibrational Schrödinger Equation in Internal Coordinates: Theory and Test Applications[†]

Jernej Stare

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia

Gabriel G. Balint-Kurti*

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

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A derivation of the vibrational Hamiltonian in generalized (internal) coordinates within a grid representation using the Fourier Grid Hamiltonian (FGH) method is presented. The objective of the theory is to make possible the solution of vibrational problems in two or more dimensions in terms of internal coordinates. These coordinates are often the ones of choice when the vibrations of interest are localized or when only selected coordinates are considered in a larger system. As in the case of the original FGH method, the matrix elements are easy to evaluate in a fast and robust manner. The method is tested on two different molecular systems, FHF^- and picolinic acid *N*-oxide, both containing strong hydrogen bonds. The illustrative problems are two-dimensional and are highly anharmonic. The importance of both the coupling terms, as well as the variable reduced masses, required by the formulation of the Hamiltonian in generalized coordinates, are examined, and the formalism is shown to be robust in that identical results are obtained using different sets of internal coordinates applied to the same physical problem. Good agreement between calculated and observed vibrational frequencies is also obtained.

I. Introduction

Hydrogen bonds are known to be highly anharmonic, and in general, a normal mode harmonic treatment of the vibrations of such bonds does not yield reliable results for the vibrational frequencies. An improved treatment, beyond the harmonic approximation, requires a more exact solution of the time-independent vibrational Schrödinger equation (SE). When the vibrational motion is localized or when we wish to restrict the analysis of the problem to a subset of the total number of degrees of freedom, it is often most convenient to perform the dynamics in terms of local internal coordinates. The ab initio calculation of the potential energy surface in such a case is best performed in the same internal coordinates. The disadvantage in using generalized local coordinates as compared with Cartesian or normal mode coordinates lies in the complexity of the form of the kinetic energy operator.[1−3] This operator contains both mixed derivative terms and a *G* matrix, which may be viewed as a set of coordinate-dependent reduced masses.

The Fourier grid Hamiltonian[4] (FGH) method was introduced in 1989 and has proved a remarkably easy and robust method for computing the vibrational motion of one-dimensional systems.[5−8] Two maintained Internet web sites[9,10] are available where a computer code based on the method can be used to solve one-dimensional vibrational problems. A modified form of the method has been suggested,[11] and it has been extended to three dimensions.[12] A "mapped" version of the method, suitable for calculations involving long range and Coulomb forces, has been developed[13] and extensively used.[14−17] The FGH method has been used in conjunction with complex optical potentials[18] to calculate predissociation line widths and in conjunction with complex scaling methods to study multiphoton above threshold dissociation.[19] Webb and Hammes-Schiffer[20] have developed a multiconfigurational self-consistent-field version of the method and have applied it to hydrogen tunneling problems. The method has been used in conjunction with time-dependent quantum theory to study photodissociation processes,[21,22] in conjunction with R-matrix theory to develop a new L^2 approach to scattering theory[23,24] and to study methods of stabilizing Feschbach resonances to form ultracold molecules.[25] In the present paper, we seek to extend the method so that it may be used in conjunction with generalized internal coordinates and, in principle, for any number of dimensions.

The theory needed for the generalization of the FGH method is developed in section II. Some discussion concerning the calculation of the *G* matrix (or the coordinate-dependent reduced masses) is also given in this section. Section III describes two test problems, both involving strong intramolecular hydrogen bonds, which are known to be highly anharmonic and require an accurate solution of the SE for their correct description. They are respectively (i) the hydrogen difluoride anion and (ii) picolinic acid *N*-oxide. Both examples involve the solution of a two-dimensional vibrational problem in several different sets of generalized internal coordinates, the different sets of coordinates giving rise to different mixed derivative terms and *G* matrices. Section IV presents the results of our test calculations using the generalized FGH method and compares results for the same system carried out using different coordinates. Section V presents some concluding remarks.

II. Theory

A. Schrödinger Equation in Generalized Coordinates. The formalism for transforming the quantum Hamiltonian operator

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* To whom correspondence should be addressed. E-mail: Gabriel.Balint-Kurti@Bristol.ac.uk.

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from Cartesian coordinates to generalized coordinates was first proposed by Podolsky in 1928.[1] For recent critical discussion concerning the problem of coordinate transformation, see Schaad and Hu.[3]

The vibrational Schrödinger equation can be written in terms of Cartesian coordinates of the atoms, $\{x\}$, where $\{x\} \equiv x_i$, $i = 1, ..., 3N$, and N is the number of nuclei involved in the vibrational problem. The corresponding Hamiltonian is

$$\hat{H}_x = -\frac{\hbar^2}{2}\sum_{i=1}^{3N}\frac{1}{m_i}\frac{\partial^2}{\partial {x_i}^2} + V \tag{1}$$

where m_i is the mass of the nucleus associated with the i^{th} Cartesian coordinate and V is the potential energy. The subscript x on the symbol $\hat{H}_x$ refers to the coordinate system in which the operator is represented (e.g., Cartesian). We will use this notation for other coordinate systems as well. This paper is concerned with the use of a grid representation, and the potential energy operator is a simple multiplicative operator in such a representation. From now on, therefore, our attention will be focused on the kinetic energy operator.

Besides atomic Cartesian coordinates, which are clearly the simplest from a mathematical viewpoint, there are other coordinates, such as the normal or internal coordinates, which are much more suitable for treating vibrational problems. The challenge is then to rewrite eq 1 for a set of generalized coordinates, $\{q\}$, which should include internal coordinates such as interatomic distances, valence and torsional angles, as well as normal coordinates, symmetry coordinates, or coordinates of any other type. Podolsky[1] showed that the kinetic energy operator, represented in a general set of coordinates $\{q\}$, should take the form:

$$\hat{T}_q = -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}\left[j^{-1/2}\frac{\partial}{\partial q_r}\left[j\cdot G^{rs}\frac{\partial}{\partial q_s}[j^{-1/2}]\right]\right] \tag{2}$$

In the above equation, j is the determinant of the Jacobian transformation matrix between $\{x\}$ and $\{q\}$, $j = \det|J_{ij}|$, where $J_{ij} = \partial x_i/\partial q_j$. M is the number of coordinates taken into account and G^{rs} is the element of the kinetic energy matrix, introduced by Wilson[2] (also known as G matrix), and is equal to:

$$G^{rs} = \sum_{i=1}^{3N}\frac{1}{m_i}\frac{\partial q_r}{\partial x_i}\frac{\partial q_s}{\partial x_i} \tag{3}$$

The G matrix is symmetric, $G^{sr} = G^{rs}$, and its matrix elements may be regarded as corresponding to reciprocal reduced masses. Unlike its Cartesian analogue, the kinetic energy operator in eq 2 includes mixed second derivatives, known as kinetic coupling terms. Moreover, all of the terms j, $j^{-1/2}$, and G^{rs} are, in general, functions of the coordinates in the set $\{q\}$; thus, they should be included in the differentiation. If we assume[26] that the coordinate dependence of the Jacobian determinant, j, is much smaller than the dependence of a particular individual component G^{rs}, eq 2 takes on the simplified form:

$$\hat{T}_q \simeq -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}\frac{\partial}{\partial q_r}\left[G^{rs}\frac{\partial}{\partial q_s}\right] \tag{4}$$

A further approximation could be to assume that the elements of the Wilson G matrix are constant. The resulting kinetic energy operator is:

$$\hat{T}_q \simeq -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}G^{rs}\frac{\partial^2}{\partial q_r \partial q_s} \tag{5}$$

Alternatively, one could still retain the coordinate dependence of the Wilson G-matrix elements, but neglect the kinetic coupling terms; hence, by omitting the mixed second derivatives from eq 4, we obtain:

$$\hat{T}_q \simeq -\frac{\hbar^2}{2}\sum_{r=1}^{M}\frac{\partial}{\partial q_r}\left[G^{rr}\frac{\partial}{\partial q_r}\right] \tag{6}$$

Finally, we may combine both the "*constant-G*" and the "*no kinetic coupling*" approximation, yielding practically the same expression as for the Hamiltonian expressed in Cartesian coordinates (eq 1):

$$\hat{T}_q \simeq -\frac{\hbar^2}{2}\sum_{r=1}^{M}G^{rr}\frac{\partial^2}{\partial {q_r}^2} \tag{7}$$

Among the possible levels of simplification of the original Podolsky expression for the kinetic energy operator (eq 2), the one yielding eq 4 is reasonable and generally acceptable. This is, however, not always true for the "*constant-G*" or for the "*no kinetic coupling*" approximation (eqs 5−7) (vide infra). When discussing techniques for solving the Schrödinger equation, we will, if not otherwise stated, use the kinetic energy operator given in eq 4. Note also that, although we will apply our treatment to handle vibrational problems in terms of internal coordinates, any other type of coordinate may be used in the approach we develop below. Furthermore, the treatments we develop in this paper for a FGH representation of the approximate forms of the kinetic energy operator represented by eqs 4−7 may readily be generalized to encompass also the exact form of eq 2, which may be needed if the approximate forms give rise to significant errors.

B. Fourier Grid Hamiltonian Method in Generalized Coordinates. The original derivation of the FGH method[4] was based on the formalism of Dirac[28] in which the operators could be expressed in either the coordinate, or Schrödinger, representation or in the momentum representation. The transformations between these two representations constituted a key aspect of this derivation. The theory outlined in the preceding section (i.e., eqs 1−7) is expressed within the Schrödinger representation, and for consistency, we will remain within this representation in the derivation given here.

We will concentrate on the form of the kinetic energy operator given in eq 4 and on its action on a wave function. The term on the right-hand side of the summation signs in eq 4 involves only two active coordinates at a time, though G^{rs} is a function of all of the coordinates. We first consider the action of a partial differential operator on a wave function. We will need to use the Fourier representation of the Dirac delta function.[28,29] This is:

$$\delta(x' - x) = \frac{1}{2\pi}\int_{k=-\infty}^{\infty} \mathrm{e}^{-ik(x'-x)}\,\mathrm{d}k \tag{8}$$

where we have taken the range of k to be $-\infty \leq x \leq +\infty$ and we will take the range of x to be $0 \leq x \leq \infty$.

$$\begin{aligned}\frac{\partial}{\partial x}\psi(x) &= \frac{\partial}{\partial x}\int_{x'=0}^{\infty}\delta(x'-x)\psi(x')\,\mathrm{d}x' \\ &= \frac{\partial}{\partial x}\int_{x'=0}^{\infty}\left\{\frac{1}{2\pi}\int_{k=-\infty}^{\infty}\mathrm{e}^{-ik(x'-x)}\,\mathrm{d}k\right\}\psi(x')\,\mathrm{d}x' \\ &= \int_{x'=0}^{\infty}\left\{\frac{1}{2\pi}\int_{k=-\infty}^{\infty}ik\mathrm{e}^{-ik(x'-x)}\,\mathrm{d}k\right\}\psi(x')\,\mathrm{d}x' \qquad (9)\end{aligned}$$

We will now discretize both k and x on uniform grids. We will use an odd number of grid points as this is needed to obtain a real form for the matrix representation of the first derivative operator (eq 9) in the grid representation. If the length of the coordinate grid is taken to be L and there are N grid points (note N is odd), the grid spacing is given by $\Delta x = L/N$ and the value of the coordinate for the j^{th} grid point is given by $x_j = j\Delta x$.

The spacing in the momentum grid is given by[30] $\Delta k = 2\pi/L$. The values of k are evenly distributed about zero, ranging from $k = -n\Delta k$ to $k = +n\Delta k$, where $n = (N - 1)/2$. Using all of these definitions, we can write the value of the partial differential at the jth grid point as:

$$\begin{aligned}\left[\frac{\partial}{\partial x}\psi(x)\right]_{x=x_j} &= \sum_{t=1}^{N}\left\{\frac{1}{2\pi}\sum_{p=-n}^{n}ip\Delta k\mathrm{e}^{-ip\Delta k(t-j)\Delta x}\Delta k\right\}\psi_{\mathrm{t}}\Delta x \\ &= \sum_{t=1}^{N}\left\{\frac{2\pi}{L^2}\sum_{p=-n}^{n}ip\mathrm{e}^{-i2\pi p(t-j)/N}\right\}\psi_{\mathrm{t}}\Delta x \\ &= \sum_{t=1}^{N}\left\{-\frac{2\pi}{L^2}\sum_{p=1}^{n}ip\left[\mathrm{e}^{i2\pi p(t-j)/N} - \mathrm{e}^{-i2\pi p(t-j)/N}\right]\right\}\psi_{\mathrm{t}}\Delta x \\ &= \sum_{t=1}^{N}\left\{-\frac{4\pi}{LN}\sum_{p=1}^{n}p\sin[2\pi p(j-t)/N]\right\}\psi_{\mathrm{t}} \qquad (10)\end{aligned}$$

where $\psi_t = \psi(x_t)$ and we can identify the term in braces, which is the $(j, t)^{\text{th}}$ element of a matrix, as the grid representation of the first derivative operator. We can therefore write:

$$\left[\frac{\partial}{\partial x}\right]_{j,t} = \left\{-\frac{4\pi}{LN}\sum_{p=1}^{n}p\sin[2\pi p(j-t)/N]\right\} \qquad (11)$$

The summation in eq 11 may be performed analytically (see eq 1.352 of ref 31) to yield:

$$\left[\frac{\partial}{\partial x}\right]_{j,t} = \begin{cases} 0 & \text{for } j = t \\ -\frac{2\pi}{LN}\left[\frac{\sin[(n+1)(j-t)2\pi/N]}{2\sin^2[(j-t)\pi/N]} + \frac{(-1)^{j-t+1}(n+1)}{\sin[(j-t)\pi/N]}\right] & \text{for } j \neq t \end{cases} \qquad (12)$$

A similar derivation leads to the following expression for the grid representation of the second derivative:

$$\left[\frac{\partial^2}{\partial^2 x}\right]_{j,t} = \begin{cases} -\left(\frac{2\pi}{L}\right)^2\frac{n(n+1)}{3} & \text{for } j = t \\ -\left(\frac{2\pi}{L}\right)^2\frac{1}{2N\sin^2[(t-j)\pi/N]}[(-1)^{t-j}(n+1)\cos[(t-j)\pi/N] + \\ \quad (n+1)\cos[(n+1)(t-j)2\pi/N] - \\ \quad \sin[(n+1)(t-j)2\pi/N]\cot[(t-j)\pi/N]] & \text{for } j \neq t \end{cases} \qquad (13)$$

We can now address the form of the grid representation of the "*variable-G*" form of the kinetic energy operator (eq 4). The grid representation of this operator can be written as

$$\begin{aligned}T_{\mu_1,...,\mu_M;\mu'_1,...,\mu'_M} &= \\ -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}\Bigg\{\delta_{rs}\sum_{l=1}^{N_{\mathrm{r}}}&\left[\frac{\partial}{\partial q_r}\right]_{q_{r,\mu_r};q_{r,l}}\left[\frac{\partial}{\partial q_r}\right]_{q_{r,l};q_{r,\mu'_r}}G^{rs}(q_{r,l}, q_{s,\mu_s}; q_{i,\mu_i}) + \\ (1-\delta_{rs})&\left[\frac{\partial}{\partial q_r}\right]_{q_{r,\mu_r};q_{r,\mu'_r}}\left[\frac{\partial}{\partial q_s}\right]_{q_{s,\mu_s};q_{s,\mu'_s}} \times \\ &G^{rs}(q_{r,\mu'_r}, q_{s,\mu_s}; q_{i,\mu_i})\Bigg\}\prod_{i\neq r,s}^{M}\delta_{\mu_i\,\mu'_i} \qquad (14)\end{aligned}$$

The notation q_{r,μ_r} indicates the grid point μ_{r} of the coordinate q_{r} and $G^{rs}(q_{r,\mu'_r}, q_{s,\mu_s};q_{i,\mu_i})$ indicates that, among the arguments of G^{rs}, the q_{i,μ_i} term stands for all of the coordinates other than the "running" coordinates q_r and q_s, i.e., $i \neq r, s$. Similarly, the grid representation of the kinetic energy operator for the "*constant-G*" approximation (see eq 5) takes the form

$$\begin{aligned}T_{\mu_1,...,\mu_M;\mu'_1,...,\mu'_M} = -\frac{\hbar^2}{2}\sum_{r=1}^{M}\sum_{s=1}^{M}\Bigg[&\delta_{rs}G^{rs}\left[\frac{\partial^2}{\partial^2 q_r}\right]_{q_{r,\mu_r};q_{r,\mu'_r}} + \\ &(1-\delta_{rs})G^{rs}\left[\frac{\partial}{\partial q_r}\right]_{q_{r,\mu_r};q_{r,\mu'_r}}\left[\frac{\partial}{\partial q_s}\right]_{q_{s,\mu_s};q_{s,\mu'_s}}\Bigg] \times \prod_{i\neq r,s}^{M}\delta_{\mu_i\,\mu'_i} \qquad (15)\end{aligned}$$

The grid representation of the potential energy is just the potential energy evaluated at the grid points:

$$V_{\mu_1,...,\mu_M;\mu'_1,...,\mu'_M} = V(\mathrm{q}_{1,\mu_1},..., q_{M,\mu_M})\prod_{i=1}^{M}\delta_{\mu_i\mu'_i} \qquad (16)$$

The overall Hamiltonian in the grid representation is then just the sum of the kinetic energy and the potential energy terms (i.e., eqs 14 plus 16 or eqs 15 plus 16. The vibrational eigenvalues and eigenfunctions are obtained by diagonalizing this grid representation of the Hamiltonian matrix. The resulting eigenvectors, ψ_λ, are normalized according to:

$$\sum_{\mu_1...\mu_M}|\psi_\lambda(q_{1,\mu_1}, q_{2,\mu_2}, ...q_{M,\mu_M})|^2 = 1 \qquad (17)$$

The dimensionality of the vibrational problem can pose severe limitations to the applicability of this approach to problems involving more than a few dimensions. It is at present difficult to treat a vibrational problem in more than two dimensions by using the above generalized FGH method because of the limitations of computer memory. Although it is possible to overcome this limitation by using iterative diagonalization techniques,[32] the problem of evaluating the potential energy surface (normally by pointwise ab initio or density functional theory (DFT) calculations) remains a bottleneck and normally limits the number of dimensions that can still be treated by this approach to about six.

C. Calculation of G^{rs}. The evaluation of the G matrix, eq 3, requires a knowledge of the mutual dependence between the Cartesian and the internal coordinates. Clearly, the G^{rs} elements will in general be functions of the internal coordinates. To account for this functional dependence, one needs to evaluate the G^{rs} functions over some appropriate range of the internal coordinates of interest. From eq 3, it follows that the dependence of the internal coordinates q_r and q_s on the complete set of Cartesian coordinates must be known in order to calculate a particular G^{rs} function and its derivatives. The most practical way of doing this is to extract the system geometries simultaneously with the pointwise determination of the potential energy function.

To deal with a pure vibrational problem, one needs to remove translational and rotational degrees of freedom from the overall nuclear motion. This can be done by enforcing the Eckart[33] conditions for each nuclear conformation of the system considered. Each particular conformation is translated and rotated with respect to the reference structure (which may be, but is not necessarily, the minimum energy structure) in order to satisfy the following equations of constraint

$$\sum_{\alpha=1}^{N} m_\alpha(\mathbf{d}_\alpha \cdot \mathbf{r}_\alpha^0) = 0 \tag{18}$$

$$\sum_{\alpha=1}^{N} m_\alpha(\mathbf{d}_\alpha \times \mathbf{r}_\alpha^0) = 0 \tag{19}$$

In the expressions above, $\mathbf{r}_\alpha^0$ denotes the position vector of the α^{th} atom in the reference geometry with respect to the center of mass of the system, and $\mathbf{d}_\alpha$ is the displacement vector of the α^{th} atom from its position in the reference geometry. Note that the product in eq 18 is the dot (scalar) product of vectors $\mathbf{d}_\alpha$ and $\mathbf{r}_\alpha^0$, whereas that in eq 19 is the cross (vector) product.

Having ensured that all of the displacements conform to the Eckart conditions, one can evaluate the derivatives of the type $\partial q_r/\partial x_i$ and calculate the G-matrix elements by using eq 3. As an alternative to doing this, it is possible to first calculate the elements of the inverse of the G matrix, G_{rs}, where:

$$G_{\text{rs}} = \sum_{i=1}^{3N} m_i \frac{\partial x_i}{\partial q_r} \frac{\partial x_i}{\partial q_s} \tag{20}$$

The values of G^{rs} are then obtained by inverting the matrix of G_{rs}. This procedure is based on that introduced by Alexandrov et al.[34] The main advantage of this approach, as compared with the direct evaluation of eq 3, is that it takes full account for the "coupling" between all possible pairs of internal and Cartesian coordinates (q_r and x_i), caused by imposing the Eckart conditions. In eq 20, the internal coordinates are the independent variables, whereas the Cartesian coordinates are the dependent variables. Evaluation of the derivative $\partial x_i/\partial q_r$ thus requires first making a small variation of the internal coordinate, δq_r, then imposing the Eckart conditions on the structure resulting from the distortion, and finally calculating the resulting change of the Cartesian coordinates, δx_i. The key point is that a variation of the internal coordinate of interest affects all of the Cartesian coordinates of the system through the imposition of the Eckart constraints. Therefore, all of the derivatives $\partial x_i/\partial q_r$ in general assume nonzero values. On the other hand, in eq 3, the Cartesian coordinates are the independent and the internal coordinates are the dependent variables. Thus, when evaluating the derivative $\partial q_r/\partial x_i$, one should first make a variation of the Cartesian coordinate, δx_i, and calculate the resulting change in the internal coordinate, δq_r, after imposing the constraints required by the Eckart conditions. Imposition of the Eckart conditions will, in this case, affect only the Cartesian coordinates but none of the internal ones and the only nonzero derivatives in eq 3 arise when the definition of q_r itself involves the Cartesian coordinate x_i. For these reasons, the application of eq 20, followed by matrix inversion, is the method of choice for the calculation of G^{rs} for pure vibrational coordinates.

III. Model Systems and Computational Details

A. Hydrogen Difluoride Anion in the Gas Phase. The hydrogen difluoride anion probably features the strongest and shortest hydrogen bond of any chemical species. The F···F separation determined from gas-phase experiments[35] is 2.2777 Å, and the hydrogen bond dissociation energy is 45.8 kcal/mol.[36] The equilibrium structure is linear with the proton located in the middle symmetrically between the fluorines.

The infrared spectrum[37] of FHF^- in the gas phase shows three fundamental bands: $\nu_1(\sigma_g^+)$ at 583 cm^{-1} (symmetric stretching), $\nu_2(\pi_u)$ at 1286 cm^{-1} (bending), and $\nu_3(\sigma_u^+)$ at 1331 cm^{-1} (asymmetric stretching). The latter was initially believed to be at a much higher frequency, 1848 cm^{-1},[35] but because of the large discrepancy with computationally determined values,[38] the band at 1848 cm^{-1} was reassigned as the $\nu_1 + \nu_3$ overtone. The infrared spectrum of the deuterated analogue (FDF^-) has been recorded and assigned in a similar way.[39] For more references to experimental studies on FHF^-, the reader is referred to ref 35. For recent ultrafast pump−probe spectroscopy studies of the FHF entity in pyridine−$(HF)_2$ complexes, see ref 40.

There have been many computational studies devoted to the FHF^- system. Analyses of the potential energy surface (PES) and the hydrogen bond dissociation energy have shown that high level ab initio methods, rather than DFT, should be used for reliable calculations, together with large basis sets of at least valence triple-zeta quality.[41−46]

The vibrational problem for the hydrogen difluoride anion has been thoroughly discussed by several authors.[47−50] Since 1972, a number of high-quality calculations, which have gone beyond the harmonic approximation, have been performed. Almlöf[47] performed a variational two-dimensional calculation of the vibrational problem for collinear FHF^- in the orthogonal symmetry coordinates ($Q_1 = r_1 - r_2$ and $Q_2 = r_1 + r_2$, where r_1 and r_2 are the two F−H distances). Janssen et al.[38] determined the vibrational levels and wave functions using normal coordinates and a three-dimensional quartic potential. A vibrational self-consistent field method[51] was first performed and was followed by a vibrational configuration interaction calculation. Špirko et al.[49] used a rather sophisticated set of rectilinear vibrational coordinates in conjunction with the Watson isomorphic Hamiltonian[52] in a three-dimensional treatment of the vibrational problem. Yamashita et al.[50] used hyperspherical coordinates combined with a mixed discrete variable-finite basis representation and applied an adiabatic separation between the "heavy-atom" (symmetric stretching) and other vibrational modes. All of the authors used PESs computed using highly correlated ab initio methods coupled with large orbital basis sets. Their findings, especially those in refs 49 and 50, are in

TABLE 1: Fitted Parameters of the Gaussian-Type Potential Energy Surface of the Linear Hydrogen Difluoride Anion[a]

i	N_i [kcal/mol]	α_i[Å^{-1}]	β_i [Å^{-1}]	$r_1^{i,0}$ [Å]	$r_2^{i,0}$ [Å]
1	688.093744	0.286313	0.757860	2.217042	0.908539
2	6025.414202	2.907677	2.904287	−0.103445	0.568055
3	3643.870535	8.151267	1.077136	−0.042802	1.240373
4	1653.010505	1.933486	735.167507	1.467196	−0.001189
5	1889.030488	0.584252	3.096505	1.806931	0.140254
6	2018.253942	2.798651	0.246531	0.429166	−2.189854
7	688.093744	0.757860	0.286313	0.908539	2.217042
8	6025.414202	2.904287	2.907677	0.568055	−0.103445
9	3643.870535	1.077136	8.151267	1.240373	−0.042802
10	1653.010505	735.167507	1.933486	−0.001189	1.467196
11	1889.030488	3.096505	0.584252	0.140254	1.806931
12	2018.253942	0.246531	2.798651	−2.189854	0.429166

[a] The analytical form reads $V(r_1, r_2) = V_c - \sum_{i=1}^{12} N_i e^{-\alpha_i^2(r_1-r_1^{i,0})^2} e^{-\beta_i^2(r_2-r_2^{i,0})^2}$, where V_c is the constant term (V_c = 12649.257711 kcal/mol), and for each particular Gaussian N_i is its coefficient, α_i and β_i are the exponential constants, and $r_1^{i,0}$ and $r_2^{i,0}$ are the coordinates of its center. The two internal coordinates r_1 and r_2 correspond to the two F−H distances.

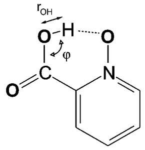

Figure 1. Structure of picolinic acid *N*-oxide (PANO) and the O−H stretching and bending internal coordinates.

good agreement with experiment and suggest a high degree of anharmonicity for the asymmetric stretching mode and strong coupling between the asymmetric stretching and bending modes. The bending mode, however, exhibits virtually no deviation from harmonicity.

The purpose of our work is not further improvement of the reliability of such calculations but rather a demonstration that vibrational problems can be reliably treated in terms of a very simple set of internal coordinates. The example of FHF$^-$ nicely illustrates the necessity of proper inclusion of the coupling terms in the kinetic energy part of the vibrational Hamiltonian.

Computational Details. The PES was evaluated by performing calculations at 422 collinear geometries of the F−H−F$^-$ system using the MP4(SDQ)/6-311++G(2d,2p) level of theory. The calculations were performed using the Gaussian 98[53] computer code, and the H−F separations, r_1 and r_2, were varied over the range 0.8−2.5 Å. The PES was fitted to an analytical function of the form $V(r_1, r_2) = V_c - \sum_{i=1}^{12} N_i e^{-\alpha_i^2(r_1-r_1^{i,0})^2} e^{-\beta_i^2(r_2-r_2^{i,0})^2}$. The 12 two-dimensional Gaussian functions in this expansion are divided into two groups of six, guaranteeing compliance with the symmetry condition $V(r_1, r_2) = V(r_2, r_1)$. All of the exponential factors (α_i,β_i), the centers of the Gaussians ($r_1^{i,0}$, $r_2^{i,0}$), the coefficients (N_i), and the constant term (V_c) were optimized using a nonlinear least squares procedure. The average fitting error was 0.0211 kcal/mol per point in the lowest 20 kcal/mol region of the PES (relative to minimum); hence, the fit was of very high quality. The parameters of the PES are listed in Table 1, and the surface is displayed in Figure 2.

Three distinct coordinate sets were used for solving the vibrational SE:

(a) $q_1 \equiv r_1$ and $q_2 \equiv r_2$;
(b) $q_1 \equiv r_1$ and $q_2 \equiv r_1 + r_2$;
(c) $q_1 \equiv r_1 - r_2$ and $q_2 \equiv r_1 + r_2$.

For each of the above $\{q_1, q_2\}$ coordinate sets, the reduced masses were calculated as follows. All of the 422 structures appearing in the pointwise calculation of the PES were represented in the center-of-mass Cartesian coordinate system, hence satisfying eq 18. Because all of these structures were linear with only x atomic coordinates assuming nonzero values, there was no need of decoupling the rotational degrees of freedom. Next, for each possible constant value of q_2, each of the atomic Cartesian coordinates x_i was 1D spline-interpolated along q_1 and the $\partial x_i/\partial q_1$ derivatives were evaluated at each of the q_1 values. The same procedure was repeated with changed roles between q_1 and q_2 in order to obtain $\partial x_i/\partial q_2$. The G_{rs} matrix elements were calculated using eq 20 for each particular structure; the G^{rs} elements were obtained by inverting the matrix of G_{rs}.

Finally, for each coordinate set, a two-dimensional grid was laid along q_1 and q_2 in such a way that at least the lowest 100 kcal/mol portion of the PES (relative to the global minimum) was completely covered by the grid and the vibrational SE was solved. The grid resolution, i.e., the number of basis functions, was optimized for the lowest 20 eigenvalues within 1 cm^{-1} precision; that is, we found the minimal grid resolution, for which the resulting 20 lowest eigenvalues differ less than 1 cm^{-1} from the reference results. The latter were obtained by using a grid of much higher resolution (101 grid points per each dimension). Typically, we found the convergent grid resolution to be about 41 by 41. In addition, we reduced the Hamiltonian matrix size by discarding the grid points with the potential energy higher than a certain threshold[11] that we set to 100 kcal/mol. By discarding the high energy region basis functions, we considerably reduced the Hamiltonian matrix size (up to 50%), and thus the CPU time required for diagonalization, without altering the lower range of the eigenvalues, relevant for vibrational spectroscopy.

B. Picolinic Acid *N*-Oxide in the Solid State. Picolinic acid *N*-oxide (PANO, Figure 1) contains a very short O−H···O hydrogen bond with an asymmetric single well proton potential. The structure of crystalline PANO has been well resolved by X-ray[54] and neutron[55] diffraction. The X-ray determined O···O distance is 2.425 Å. Infrared spectra of PANO, either in the solid state or in solution (using various solvents),[56] feature a broad absorption in the range between 1000 and 1800 cm^{-1}, which has been assigned to the O−H stretching mode. NMR studies provide additional evidence for a strong, short hydrogen bond, with the chemical shift of the hydrogen-bonded proton being about 18 ppm in solutions using different solvents.[57,58]

Recent ab initio and DFT calculations on PANO have shown that proper inclusion of the crystal field is essential to obtain reasonable agreement with experiment for the geometry of PANO, as well as for the shape of the proton potential. The O···O distance in the optimized geometry of an isolated molecule was found to be greater than 2.50 Å, no matter what level of theory was used, compared to 2.43 Å, determined by the X-ray and neutron diffraction. Introducing periodicity into DFT calculations using the Car−Parrinello method shifts the computed equilibrium O···O distance to 2.45 Å and significantly "flattens" the proton potential.[59]

A gas phase model of PANO has been found to yield results for the vibrations of the proton involved in the hydrogen bond which differ considerably from those observed experimentally in the solid state or solution. A harmonic frequency calculation for the isolated molecule at the B3LYP/6-311++G(3df,3pd) level of theory yields ν_{OH} = 2977 cm^{-1}, whereas a two-dimensional anharmonic frequency calculation along the O−H stretching and O···O stretching coordinates gives ν_{OH} = 1733

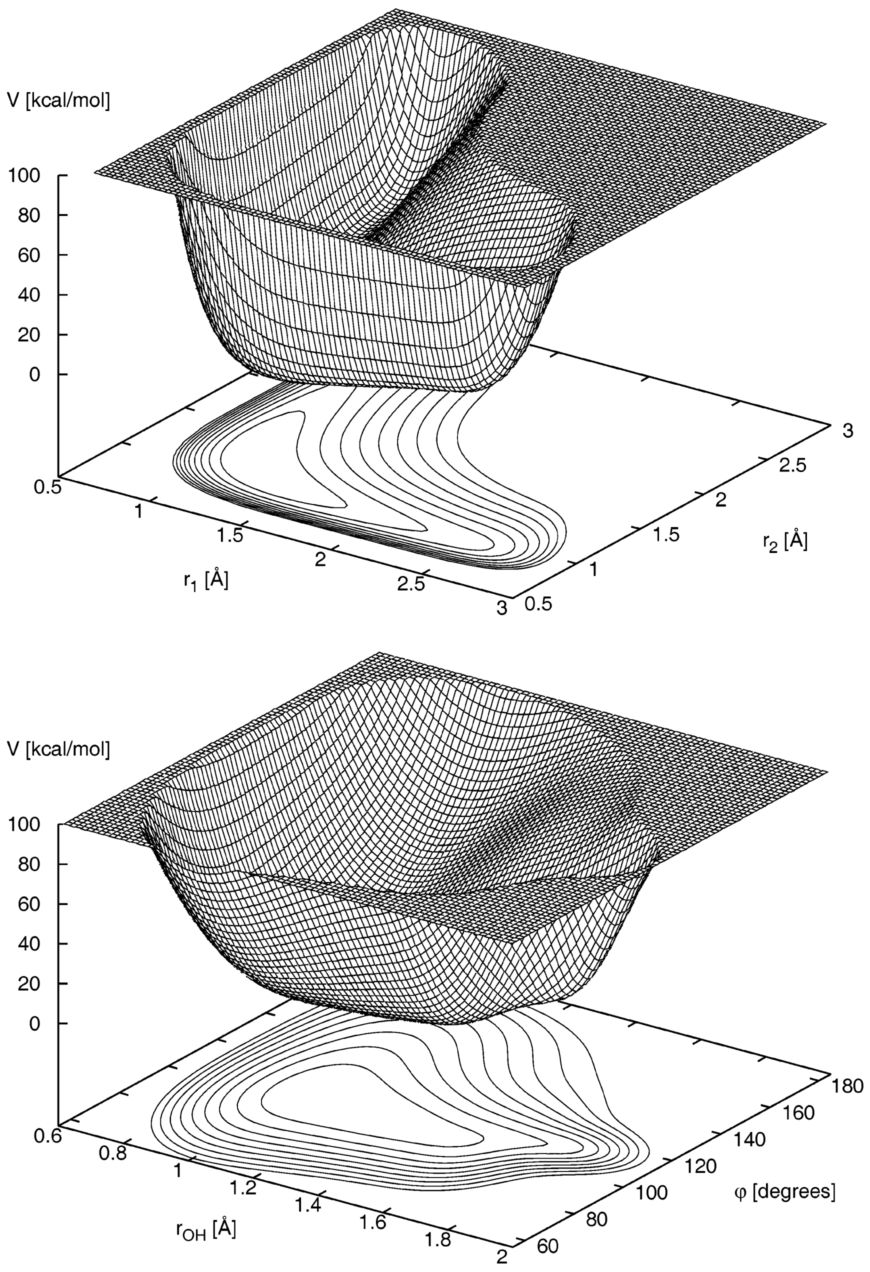

Figure 2. Potential energy surfaces (PESs) of the hydrogen difluoride anion (top) and picolinic acid *N*-oxide, PANO (bottom). The contours are drawn at each 10 kcal/mol, and the inner contour corresponds to an energy lying 10 kcal/mol above the minimum of the PES.

TABLE 2: *G*-Matrix Elements (in amu^{-1}) of Hydrogen Difluoride Anion in Three Different Coordinate Sets[a]

coordinate set	G^{11}	G^{22}	G^{12}
(a) (r_1, r_2)	1.05263 (0.55263)	1.05263 (0.55263)	−1 (−0.5)
(b) $(r_1, r_1 + r_2)$	1.05263 (0.55263)	0.10526 (0.10526)	0.05263 (0.05263)
(c) $(r_1 - r_2, r_1 + r_2)$	4.10526 (2.10526)	0.10526 (0.10526)	0 (0)

[a] The values in parentheses pertain to the deuterated analogue. See text for definition of the coordinate sets.

cm^{-1}.[60] We therefore decided to study the vibrational problem of PANO within the solid-state model. In the present study, we address the two-dimensional O−H stretching/bending vibrational problem. We have chosen the bending (δ_{OH}) mode to be the second coordinate because the bending mode, although it has not yet been well assigned, is believed to be located around 1500 cm^{-1} (i.e., quite close to the center of the broad O−H stretching mode) and may be anharmonically coupled to the O−H stretching mode. In unpublished work, we observed traces of anharmonic coupling between ν_{OH} and δ_{OH} within the gas-phase model.[61]

Computational Details. The PES was calculated, one nuclear geometry at a time, using the Car−Parrinello Molecular Dynamics program (CPMD v. 3.5.1).[62,63] A BLYP density functional coupled with a plane wave basis set with an energy cutoff of 120 Rydbergs and a relativistic Goedecker pseudopotentials were used. The periodicity of the system was fully taken into account in a way consistent with the crystallographic data.[54] The PES along the O−H distance ($q_1 \equiv r_{OH}$) and the C−O−H bending angle ($q_2 \equiv \varphi$) was evaluated for 340 nuclear geometries. r_{OH} was varied from 0.80 to 1.75 Å, whereas φ was varried between 70 and 150°. Only the proton position was

TABLE 3: Calculated and Observed Vibrational Frequencies and Zero-Point Energies of the Hydrogen Difluoride Anion (All Values in cm^{-1})[a]

level of calculation	ZPE	ν_1	ν_3	$\nu_1 + \nu_3$
full Hamiltonian[b]	961 (742)	592 (597)	1369 (935)	1891 (1470)
no coupling;[c] coordinate set (a)	1828 (1306)	2938 (2112)	896 (631)	3908 (2854)
no coupling;[c] coordinate set (b)	978 (763)	584 (580)	1411 (990)	1928 (1510)
Špirko[d]		580 (587)	1315 (919)	1814 (1443)
Morokuma[e]		595 (602)	1374 (956)	1904 (1502)
harmonic[f]	843[g] (695)	645 (644)	1041 (746)	1686 (1390)
experimental[h]		583 (588)	1331 (934)	1848 (1469)

[a] Values in parentheses pertain to deuterated analogue. Please note that the zero-point energy of a harmonic oscillator with $\hbar\omega_0 = 1000$ cm^{-1} corresponds to 500 cm^{-1} or 1.429572 kcal/mol. See text for definition of the coordinate sets. [b] With kinetic part given by eq 5. [c] With kinetic part given by eq 7. [d] Reference 49. [e] Reference 50. [f] Calculated at the MP4(SDQ)/6-311++G(2d,2p) level of theory on a previously minimized structure. [g] Taken as $1/2(\nu_1 + \nu_3)$. [h] References 37 and 39.

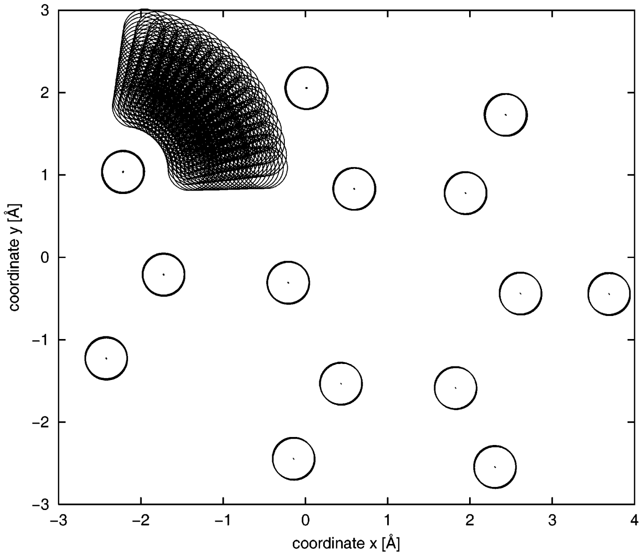

Figure 3. Overlaid structures of picolinic acid *N*-oxide, represented in the center-of-mass Cartesian coordinate system, as appearing in the calculation of the potential energy surface after elimination of translational and rotational components from the nuclear motion. The nuclei are represented as dot-centered circles. Note that the coordinate *z* assumes a value of zero throughout, because the structure is planar.

displaced, whereas the other nuclei were fixed at their equilibrium positions. A two-dimensional spline interpolation[30] scheme was used to evaluate the potential energy at the grid points needed in the dynamical calculations. The PES of PANO is displayed in Figure 2. The values of G^{rs} were determined in the same way as described for the hydrogen difluoride anion, with the difference that rotational components of the nuclear motion were eliminated by rotating each particular nuclear structure in order to satisfy the conditions of eq 19. This was done just before performing the spline interpolation of the Cartesian coordinates as a function of the internal coordinates. Figure 3 displays the overlaid structures of PANO, arising in the calculation of the PES, after elimination of translational and rotational degrees of freedom. We again use a two-dimensional spline interpolation procedure to evaluate the elements of G^{rs} at each grid point in the internal coordinate space, just as we did in the case of the potential energy surface. Finally, a grid along r_{OH} and φ was laid and optimized in the same way as in the case of the FHF$^-$, and the vibrational SE was solved. All calculations were performed on a cluster of 24 dual-CPU PC/Linux systems (AMD Athlon XP 1600+ CPUs, 512 MB of memory).

IV. Results and Discussion

A. Hydrogen Difluoride Anion. Regardless of the coordinate set, in which the vibrational problem was formulated, e.g., (a),

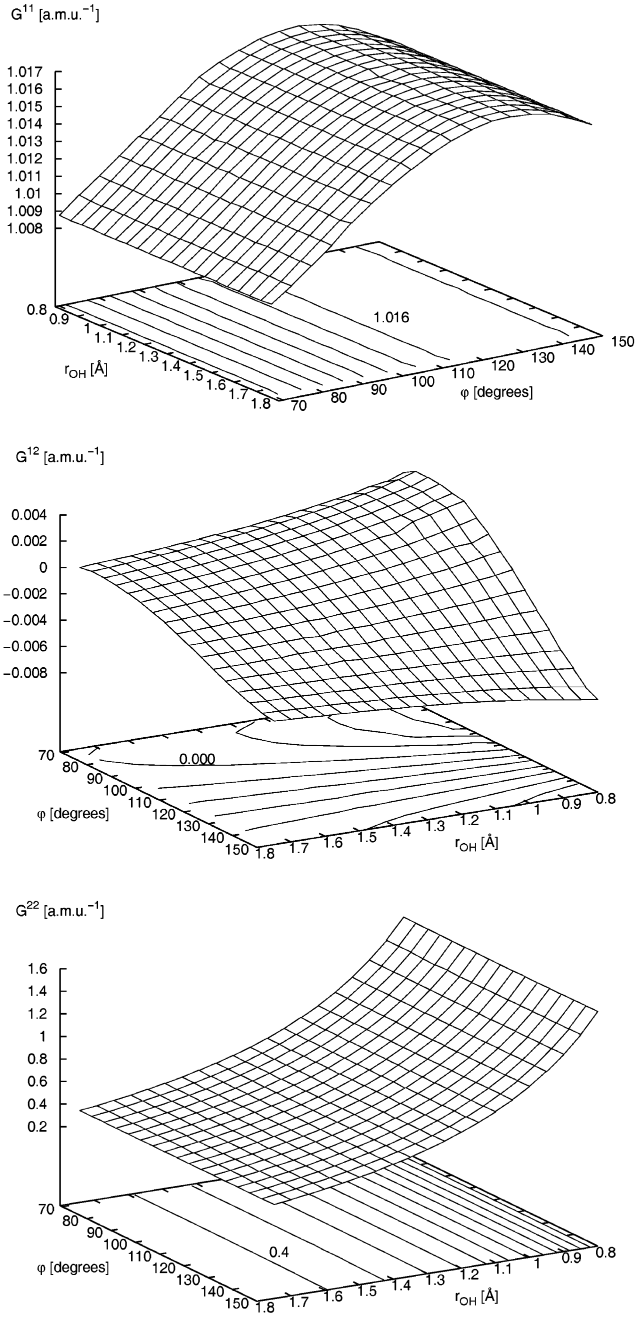

Figure 4. *G*-matrix elements (i.e., reciprocal reduced masses) of picolinic acid *N*-oxide along the stretching and bending coordinates as functions of internal coordinates. The contours of G^{11} and G^{12} are drawn at each 0.001 amu^{-1}, whereas those of G^{22} are at each 0.1 amu^{-1}. In each case, one of the contours is labeled according to its actual value.

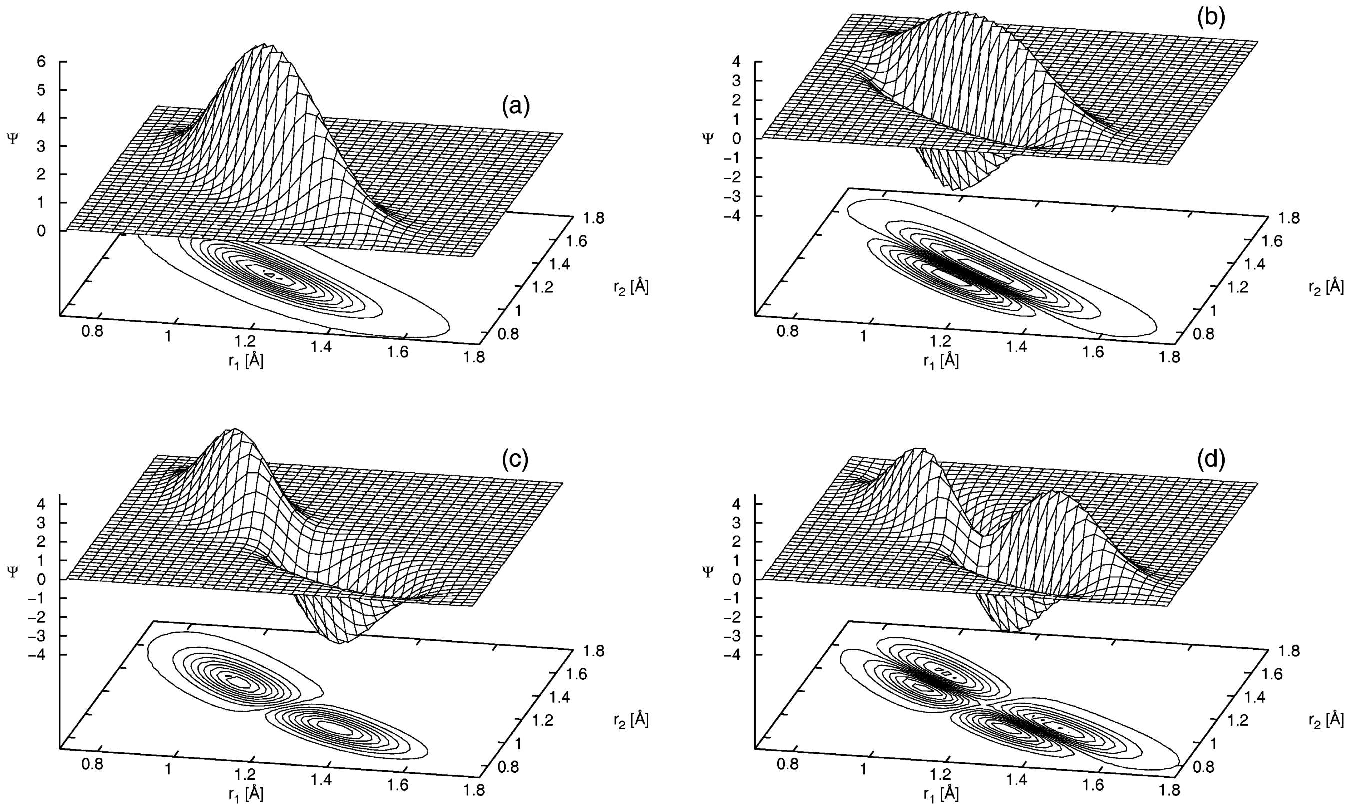

Figure 5. Vibrational wave functions of FHF$^-$: (a) ground state; (b) ν_1 excited state (symmetric stretching); (c) ν_3 excited state (asymmetric stretching); (d) combined excited state ($\nu_1 + \nu_3$ overtone).

(b), or (c), the *G*-matrix elements were found to have constant values as a function of the internal coordinates. Therefore, eq 4 for the kinetic part of the Hamiltonian of this system can be simplified to eq 5 without any loss of accuracy. The values of the *G*-matrix elements within each of the above coordinate sets are listed in Table 2. The coordinate set c is clearly orthogonal and thus free of coupling; coordinates within this set are called *symmetry coordinates* and were used by Almlöf[47] in his studies of the vibrational problem in FHF$^-$. Coordinate sets a and b are not orthogonal and include a nonzero G^{12} coupling term. This coupling term is much larger in coordinate set a than in b, especially when judged relative to the values of the diagonal elements, G^{11} and G.^{22}

Table 3 lists the vibrational frequencies computed in the present work and also gives frequencies computed by other workers for comparison. Wave functions corresponding to the eigenstates listed in Table 3 are displayed in Figure 5. All three coordinate sets (a, b and c) yield virtually identical frequencies, provided that the coupling terms were taken into account. These calculations are referred to as the "full Hamiltonian" approach in the table. The calculated frequencies compare very well both with the previous calculations and with experimental values. The table clearly shows that a normal mode harmonic treatment of the system yields completely unsatisfactory results. It overestimates ν_1 by 62 cm^{-1} and underestimates ν_3 by as much as 290 cm^{-1}.

Omission of the coupling term from the Hamiltonian, i.e., using eq 7 instead of eq 5 for the kinetic part of the Hamiltonian, shifts the calculated frequencies away from the experimental values. In the case of coordinate set b, the "no coupling" approximation still yields reasonable values for the stretching frequencies. Although ν_1 is shifted down by only 8 cm^{-1}, being by chance in even better agreement with the experimental value, ν_3 is increased by 42 cm^{-1}. For coordinate set (b) neglect of kinetic coupling still yields qualitatively correct results. In contrast, neglect of this coupling when using coordinate set (a) produces completely wrong results, leading to an increase of ν_1 by 396% and a decrease of ν_3 by 34%.

TABLE 4: Fundamental Vibrational Frequencies (in cm^{-1}) of Solid Picolinic Acid *N*-Oxide

	1D models	full Hamiltonian[b]	no coupling[c]	constant-*G*[d]	no coupling and constant-*G*[e]
ν_1	1450[f]	1299	1299	1386	1386
ν_2	1577[g]	1767	1767	1831	1831

[a] The potential energy surface was calculated at the BLYP DFT level and the periodic structure of the solid was taken into account. [b] With kinetic part given by eq 4. [c] With kinetic part given by eq 6. [d] With kinetic part given by eq 5. [e] With kinetic part given by eq 7. [f] O−H stretching frequency. [g] (C)−O−H bending frequency.

B. Picolinic Acid *N*-Oxide. Unlike the case of the FHF$^-$ ion, we found that the *G*-matrix elements for PANO displayed a considerable coordinate dependence. This is particularly the case for the dependence of G^{22} on r_{OH}. Figure 4 shows the *G*-matrix elements as functions of r_{OH} and φ. In contrast to the hydrogen difluoride anion, where the coupling term was of significant importance for some choices of the internal coordinates, in PANO, the coupling term is small and has no significant effect on the final results. G^{11} is always close to unity and G^{22} varies from 0.32 to 1.58. G^{12}, on the other hand, assumes values between −0.006 and 0.003, which may be considered negligible in comparison to the diagonal elements.

The frequencies of PANO, calculated using different approximations for the kinetic energy operator are listed in Table 4. Preliminary one-dimensional calculations along the stretching and bending coordinates yielded the frequencies of 1450 and 1577 cm^{-1} for stretching and bending, respectively. Combining these coordinates and solving the two-dimensional vibrational SE leads to a considerable shift of the frequencies. The two

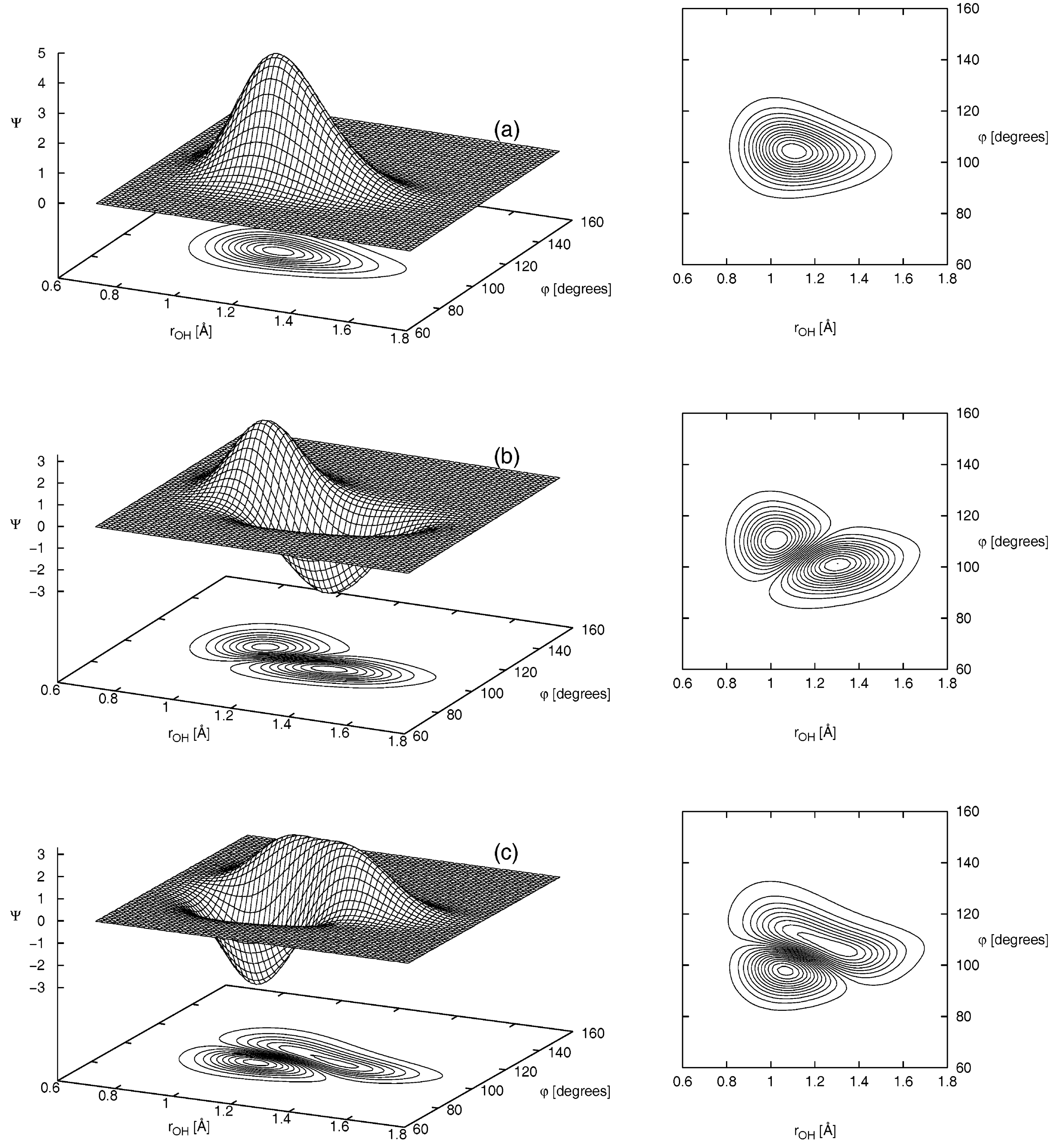

Figure 6. Vibrational wave functions of picolinic acid *N*-oxide: (a) ground state; (b) first excited state (ν_1); (c) second excited state (ν_2). The corresponding two-dimensional contour plots are added for convenience.

lowest excited states are now calculated to be at 1299 (ν_1) and 1767 cm^{-1} (ν_2) above the ground state, respectively. This corresponds to a shift of about 150 cm^{-1} downward and 190 cm^{-1} upward relative to the values obtained from the one-dimensional model calculations. However, these two excited states can no longer be clearly assigned as stretching and bending, because both excited states possess approximately equal contributions of each of these internal coordinates (see Figure 6).

In contrast to the hydrogen difluoride anion, kinetic coupling in PANO has virtually no influence on the resulting frequencies and can be omitted. On the other hand, the coordinate dependence of the G matrix is significant and has an important effect on the frequencies. If constant values of the G-matrix elements are used ($G^{11} = 1.01493$ amu^{-1}, $G^{22} = 0.91355$ amu^{-1}, $G^{12} = 0.00038$ amu^{-1}) corresponding to the equilibrium geometry, ν_1 and ν_2 are increased by 87 and 64 cm^{-1}, respectively. Nevertheless, the nature of the two excited states seems to remain unchanged: they both still have approximately equal contributions of stretching and bending coordinates. The increase of frequencies can readily be explained in the following way. The PES of PANO has a wide low-energy region at rather large O−H distances (see Figure 2); at the same time, the G^{22} term decreases significantly with the increasing O−H distance (see Figure 4). Because the *G*-matrix elements play the role of reciprocal reduced masses, this can be viewed as a substantial increase of the reduced mass with the increasing value of r_{OH}. Therefore, the system can be regarded as possessing an easily accessible region in which the reduced mass is considerably larger than at the minimum of the PES, an effect that should decrease the frequencies. Therefore, the frequencies, obtained by assuming constant values of the *G*-matrix elements, should be larger than the ones calculated by taking account of its coordinate-dependence.

Because the vibrational bands of the O−H···O moiety in PANO cannot all be fully assigned or characterized in the observed infrared spectrum,[56] we cannot easily deduce how well the calculated stretching and bending frequencies agree with the experimental data. The two frequencies of $\nu_1 = 1299$ cm^{-1} and $\nu_2 = 1767$ cm^{-1} in general fit into the broad absorption range of the observed spectrum, though the value of ν_1 seems to be somewhat low and ν_2 somewhat high. On the other hand, the value of ν_1 calculated using the "*constant-G*" approximation ($\nu_1 = 1386\ cm^{-1}$) is nearer to what is believed to be the center of the O−H stretching mode; however, the other calculated frequency of $\nu_2 = 1831$ cm^{-1} fits less well into the broad experimentally observed absorption region (1000−1800 cm^{-1}). Calculations within the present model indicate very strong anharmonic potential-energy coupling between the stretching and bending modes (the kinetic coupling is, as shown, negligible). Nevertheless, there are other relevant modes that take part in the vibrations of the O−H···O moiety. These other modes, namely, those involving O···O, C=O, and N−O motions, should be taken into account in a more complete study of the vibrations of PANO.

V. Concluding Remarks

We have developed a generalized form FGH method[4,8] which permits the use of generalized internal coordinates. In particular it allows for the inclusion of both mixed derivative terms and of coordinate dependent Wilson *G*-matrix elements,[1,2] which act as inverse coordinate dependent reduced masses. The formulation is completely general and is valid for an arbitrary number of dimensions. As with the original FGH method, the matrix elements of the kinetic energy operator are all simple analytic expressions and the potential and *G*-matrix functions must be evaluated on a multidimensional grid of evenly spaced points. After calculating the Hamiltonian matrix elements in the grid representation using the simple formulas derived above, the vibrational energy levels and wave functions may be obtained by standard diagonalization techniques.[30]

The methods we have developed were applied to two illustrative test examples, the hydrogen difluoride anion and picolinic acid *N*-oxide. Both of the test systems contain strong hydrogen bonds. In each case, we have formulated and solved a two-dimensional vibrational problem in the internal coordinates: the two F−H stretchings in the hydrogen difluoride anion and the O−H stretching and (C)-O−H bending in picolinic acid *N*-oxide. In the former case, we used three different sets of internal coordinates to illustrate that the formalism gave the same results when solved in different sets of coordinates. In the case of the hydrogen difluoride anion, it was shown to be essential to include the kinetic coupling terms (mixed derivative terms) in order to obtain correct results in some of the internal coordinate sets. For picolinic acid *N*-oxide, the *G*-matrix elements varied markedly with internal coordinates, and accurate results were only achievable if this coordinate dependence of the reduced masses was correctly taken into account. In both cases, the calculated frequencies are in reasonable agreement with the experimental data. We have also shown that a further efficiency can be achieved by eliminating grid points which correspond to potential energy values above a chosen threshold.[11]

The generalized FGH method has proved to provide a stable, fast, and robust way for the evaluation of the Hamiltonian matrix elements and for solving the vibrational Schrödinger equation. It can, in principle, be applied to vibrational problems of higher dimensionality. If this is done, the size of the matrices which must be diagonalized grows rapidly with increasing dimensionality, and alternative techniques may have to be used for the diagonalization step. In such cases, it may be necessary to resort to iterative diagonalization techniques to compute a limited number of the lowest eigenvalues.[32,64] Application of some aspects of the formalism developed herein to enhanced DVR methods, such as the potential-optimized DVR,[65,66] is also possible. The most critical, computationally limiting part of the calculation is however the necessity of evaluating the potential energy at a very large number of grid points in the internal coordinate space, because the potential energy surface should normally be evaluated pointwise by computationally expensive high-level ab initio or DFT calculations.

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