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Analysis of Local Anharmonicity Using Gaussian Model Potentials and Cartesian Oscillator Basis Sets: Example, HCN[†]

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This paper examines local anharmonic vibrations in molecules using an analysis that starts with an ab initio potential energy surface, fits a model potential constructed of Gaussian basis functions, and proceeds to a quantum mechanical analysis of the anharmonic modes using Cartesian harmonic oscillator basis functions in a variational calculation. The objective of this work is to suggest methods, with origins in nuclear and molecular (electronic) quantum mechanics, that should be useful for the accurate analysis of the local anharmonic motions of hydrogen, and perhaps other atoms or small molecular fragments, residing in molecularly complicated but otherwise harmonic environments.

1. Introduction

This paper presents an analysis of *local* anharmonic motion of atoms in molecules that is constructed largely in the spirit of nuclear (viz., shell model[1]), molecular,[2] and solid state[3] quantum mechanical calculations. The analysis is local, much as the LCAO and related approximations are local in nuclear, molecular, and solid-state electronic calculations.[2]

To begin, with HCN as the example to illustrate the approach, it is possible to determine accurate local hydrogen bond energies with reference to the harmonically semirigid framework of the remainder of the molecule (i.e., CN) using any of the variety of available ab initio quantum chemistry computational packages. It is possible next to fit the energies to a model potential function, which here is a series in the Gaussian basis functions. For HCN in particular, with $r_1 = r_{\mathrm{CH}}$, $r_2 = r_{\mathrm{NH}}$, and $r_3 = r_{\mathrm{CN}}$, the Gaussian potential has the form[29]

$$V = V_0 + \sum_{\substack{I=1,3\\ m=1,N}} A_{I,m}\mathrm{e}^{-mb_I r_I^2} + \sum_{\substack{I=1,2\\ J=I+1,3\\ m+n\le N}} B_{m,n}^{I,J}\mathrm{e}^{-mb_I r_I^2 - nb_J r_J^2} + \sum_{l+m+n\le N} C_{l,m,n}\mathrm{e}^{-lb_1 r_1^2 - mb_2 r_2^2 - nb_3 r_3^2} \quad (1.1)$$

In eq 1.1, N is the collective upper limit of the exponent, or sum of exponents, of any individual term in the potential; in the calculations reported later in the paper, the maximum polynomial order is generally taken to be $N = 10$.

Although the model potential energy function for the hydrogenic degrees of freedom, in the example HCN, is a linear combination of Gaussian basis functions raised to simple powers, alternate forms of model potential employ angle-arguments, either directly or as further arguments of transcendental functions, in addition to distance variables.[4] The use here of three bond vectors for HCN, one of which is linearly dependent, implies the law of sines. As a consequence, there are enough distance variables included in the model potential to account for angle−bend degrees of freedom.

This model potential treats each bond, including the (assumed) classical bond, CN, in the same way; there is no particular advantage in using the harmonic model, $^1/_2k(r - r_0)^2$ with k the usual force constant, in place of a Gaussian basis function in the complete model potential. In fact, generally better model potential energy fits to the original surface result if one uses the same basis functions for each bond. If, however, one plans not to include r_{CN} in the quantal, anharmonic analysis, it is computationally more efficient in the subsequent treatment to rearrange the potential into two effective bond terms the coefficients of which are r_{CN}-dependent. Thus, one has

$$V = \mathscr{B}_0 + \sum_{\substack{I=1,2\\ \mu=1,N}} \mathscr{U}_{I,\mu}\mathrm{e}^{-\mu b_I r_I^2} + \sum_{\lambda,\mu} \mathscr{B}_{\lambda,\mu}\mathrm{e}^{-\lambda b_1 r_1^2 - \mu b_2 r_2^2} \quad (1.2)$$

with

$$\mathscr{B}_0 = V_0 + \sum_{\mu} A_{3,\mu}\mathrm{e}^{-\mu b_3 r_3^2} \quad (1.3)$$

$$\mathscr{U}_{I,\mu} = A_{I,\mu} + \sum_{\nu} B_{\mu,\nu}^{I,3}\mathrm{e}^{-\nu b_3 r_3^2} \quad (1.4)$$

and

$$\mathscr{B}_{\lambda,\mu} = B_{\lambda,\nu}^{1,2} + \sum_{\nu} C_{\lambda,\mu,\nu}\mathrm{e}^{-\nu b_3 r_3^2} \quad (1.5)$$

The matrix elements in the quantum mechanical analysis of anharmonicity therefore make use of eq 1.2.

Finally, in any quantum mechanical analysis of the motions of hydrogen in a molecule, there is the question of the choice of expansion/reference points. A natural point of reference is the point of (mechanical) equilibrium with respect to the heavier atom to which hydrogen is attached. Working with such a reference, one naturally adopts a sequence of bond and angle coordinates suitable to the molecule involved. There has been much work using this approach.[4] On the other hand, for the analyses of systems in which hydrogen, in particular, may migrate via a series of local minima in a large and extended molecule there is no reason not to consider these minima in terms of Cartesian and difference coordinates that refer implicitly to or are compatible with the overall collection of atoms.[5−7]

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This approach specifically considers the displacement of the hydrogen atom with reference to an equilibrium point of reference in the molecule. Indeed, this general approach allows one to choose a point of reference to be a variational parameter, should one wish.

The matrix elements of the kinetic and potential energy operators for anharmonic hydrogen are evaluated in terms of basis functions, each function of which is a product of three one-dimensional Cartesian harmonic oscillator basis functions. The coordinate origin of the wave function is also the point of (mechanical) equilibrium. Thus, the wave function depends on the displacement vector $\mathbf{r} = \mathbf{r}_{\mathrm{H}} - \mathbf{r}_A$ where $\mathbf{r}_A$ is the vector location of the point of equilibrium, $\mathbf{r}_{\mathrm{H}}^0$, or arbitrary point expansion.[7]

A particular matrix element of the potential operator, eq 1.2, is

$$\langle \mathbf{m}|V|\mathbf{n}\rangle = \mathscr{B}_0\delta_{\mathbf{m},\mathbf{n}} + \sum_{\substack{I=1,2\\ \mu=1,N}} \mathscr{U}_{I,\mu}\langle \mathbf{m}|\mathrm{e}^{-\mu b_I r_I^2}|\mathbf{n}\rangle + \sum_{\lambda,\mu} \mathscr{B}_{\lambda,\mu}\langle \mathbf{m}|\mathrm{e}^{-\lambda b_1 {r_1}^2 - \mu b_2 {r_2}^2}|\mathbf{n}\rangle \quad (1.6)$$

Because of the contraction properties of Gaussian basis functions, the second bond-bond interaction term can be expressed as an effective one-bond term. This property affords considerable simplification.

It is clear from the expression for the matrix elements, eq 1.6, that one can extract the value of the harmonic force constant for the CN bond by direct differentiation with respect to r_{CN}. Both the coefficients in the potential, eq 1.2, and the matrix elements of the Gaussian terms depend on this variable. As a consequence, the harmonic vibrations of CN will be influenced by the quantum mechanical character of the anharmonic H−C and H−N bonds.

The next section presents the one-dimensional variant of the Brody−Jacob−Moshinsky[8] (BJM) coefficients for the Cartesian harmonic oscillator basis functions. These coefficients find use in the evaluation of matrix elements of operators such as eq 1.2. The evaluation of the Talmi integrals[9] that naturally arise from the BJM analysis is presented next. A closed form for the Talmi integral follows easily from common Gaussian integral forms, but it is demonstrated that a much more efficient evaluation of a set of integrals follows with the use of recursion relations. Finally, the results of a calculation of the HC−HN stretch modes and the H−CN angle bend are presented. The results point the way to more complex analyses of the behavior of hydrogen in more complicated molecular settings.

2. Evaluation of Matrix Elements

2.1. Brody—Jacob—Moshinsky Coefficients and Talmi Integrals for 1D Oscillator Functions. The strength of the original BJM analysis[8] of matrix elements (which applies to the spherical oscillator basis functions) lies with the observation that one of the two summations involving the Laguerre polynomials in a matrix element can be carried out once, for all time, to define new coefficients. These new coefficients then can be used repeatedly for the evaluation of the remaining summation for any legitimate operator. This situation also applies to the 1D oscillator whose matrix elements depend on the Hermite polynomials. As noted, for local vibrational and related problems in molecular systems, the one-dimensional BJM coefficients should useful.[30]

The normalized one-dimensional Cartesian wave functions that satisfy the Schrödinger equation for the harmonic oscillator model potential are

$$\phi_m(\sqrt{a}x) = \sqrt{\frac{\sqrt{a}}{2^m m!\sqrt{\pi}}}\, H_m(\sqrt{a}x)\mathrm{e}^{-(1/2)ax^2} \quad (2.1)$$

The Hermite polynomials are

$$H_m(\sqrt{a}x) = \sum_{s=0}^{[m/2]}(-1)^s \frac{m!}{(m-2s)!s!}(2\sqrt{a}x)^{m-2s} \quad (2.2)$$

where as usual, $[m/2]$ implies the integer nearest to $m/2$. The normalized eigenfunctions may be written as

$$\phi_m(\sqrt{a}x) = \sum_{s=0}^{[m/2]} A_{m,s}(\sqrt{a}x)^{m-2s}\mathrm{e}^{(-1/2)ax^2} \quad (2.3)$$

with the coefficients $A_{m,s}$ defined by

$$A_{m,s} = \sqrt{\frac{2^m m!}{\sqrt{\pi}}}\,\frac{(-1)^s}{2^{2s}(m-2s)!s!} \quad (2.4)$$

Given an operator $F(x)$, a general matrix element in terms of this representation of the wave functions is

$$\langle m|F(x)|n\rangle = \sum_{s=0}^{[m/2]}\sum_{t=0}^{[n/2]} A_{m,s}A_{n,t} \times \int_{-\infty}^{\infty} \mathrm{d}x\, (\sqrt{a}x)^{m+n-2(s+t)}F(x)\mathrm{e}^{(-1/2)ax^2} \quad (2.5)$$

In the sense suggested by Moshinsky et al.,[8] let

$$2p = m + n - 2(s + t) \quad (2.6)$$

The maximum value of p is

$$\max(p) = \frac{1}{2}(m + n) \quad (2.7)$$

and

$$\min(p) = \max(p) - [m/2] - [n/2] \quad (2.8)$$

The index t can be replaced by $t = {}^1/_2(m + n) - p - s$. Thus,[31]

$$B(m, n, p) = \Gamma(p + {}^1/_2)\sum_{s=0}^{[m/2]} A_{m,s}A_{n,(1/2)(m+n)-p-s} \quad (2.9)$$

subject to

$$0 \le \max(p) - p - s \le [n/2] \quad (2.10)$$

If $F(x)$ is even, then $m + n =$ even and p is an integer. On the other hand, if $F(x)$ is odd, then $m + n =$ odd, and p is ${}^1/_2$-integer, as is also the case with the spherical oscillator functions.

With the definition of the one-dimensional Talmi integral[9,14,15]

$$T_p = \frac{a^{p+(1/2)}}{\Gamma\left(p + \frac{1}{2}\right)}\int_{-\infty}^{\infty} \mathrm{d}x\, x^{2p}F(x)\, \mathrm{e}^{(-1/2)x^2} \quad (2.11)$$

the matrix element of the operator $F(x)$ is

$$\langle m|F(x)|n\rangle = \sum_{p=\min(p)}^{\max(p)} B(m, n, p)T_p \tag{2.12}$$

The use of the Γ function in eq 2.11 follows Moshinsky's[8,16] practice for the three-dimensional case and normalizes the integral for the case of the unit operator $F(x) = 1$.

It is not necessary to list these coefficients as they are easily coded and compute quickly to high order.

2.2. 1D Talmi Integrals for the Operator e^{-bx^2}. If x in the operator $F(x) = e^{-bx^2}$ is the same as the argument of the wave function, the 1D Talmi integral is trivial: $T_p = (a/(a + b))^{p+(1/2)}$.[14]

When the coordinate argument of the operator differs from that of the wave function, the following analysis applies. For example, let $x_H - X_A$ be the displacement of hydrogen (or an appropriate atom) from a position of reference or equilibrium X_A. The argument x_B of the operator $e^{-bx_B^2}$ now is the instantaneous distance between the hydrogen and an external source, such as the carbon or nitrogen atom, $x_H - X_B$ [with, for example, B → C or N].[32] The Talmi integral is now slightly more involved.

The matrix element of the operator $e^{-bx_B^2}$ is

$$\langle m|e^{-bx_B^2}|n\rangle = \sum_p B(m, n, p)T_p\{e^{-bx_B^2}\} \tag{2.13}$$

Noting that $x_A = x - X_A$ and $x_B = x - X_B$, the Talmi integral[33] is

$$T_p\{e^{-bx_B^2}\} = \frac{a^{p+(1/2)}}{\Gamma\left(p+\frac{1}{2}\right)}\int_{-\infty}^{\infty} dx_A\, x_A^{2p}\exp(-ax_A^2 - bx_B^2) = \frac{a^{p+(1/2)}}{\Gamma\left(p+\frac{1}{2}\right)}\exp\left(-\frac{ab}{a+b}X_{BA}^2\right) \times \int_{-\infty}^{\infty} dx_A\, x_A^{2p}\exp\left(-(a+b)\left(x_A - \frac{b}{a+b}X_{BA}\right)^2\right) = \frac{a^{p+(1/2)}}{\Gamma\left(p+\frac{1}{2}\right)}\exp\left(-\frac{as}{a+b}X_{BA}^2\right) \times \sum_{j=0}^{[p]}\binom{2p}{2j}\left(\frac{b}{a+b}X_{BA}\right)^{2(p-j)}\frac{\Gamma\left(j+\frac{1}{2}\right)}{(a+b)^{j+(1/2)}} \tag{2.14}$$

and $X_{BA} = X_B - X_A$.

2.3. Recurrence Relations for the Talmi Integral for the Operator $e^{-bx_B^2}$. While the results of the last section are correct and work, the summation over j in eq 2.14 is not particularly efficient. This is especially true when compared to the use of the direct evaluation of the matrix elements following the lines of earlier work.[7]

The general one-dimensional Talmi integral is defined by eq 2.11. The particular Talmi integral, for which the recurrence relation will be developed, is defined in the first line of eq 2.14. Integrating by parts yields

$$T_p\{e^{-bx_A^2}\} = \frac{a^{p+(1/2)}}{\Gamma\left(p+\frac{1}{2}\right)}\int_{-\infty}^{\infty} dx_A\, x_A^{2p}\exp(-ax_A^2 - bx_B^2) = \frac{a^{p+(1/2)}}{\Gamma\left(p+\frac{1}{2}\right)}\left\{\frac{x_A^{2p+1}}{2p+1}\exp(-ax_A^2 - bx_B^2)\Big|_{-\infty}^{\infty} + \frac{2}{2p+1}\int_{-\infty}^{\infty} dx_A\,((a+b)x_A - bx_{BA})x_A^{2p+1} \times \exp(-ax_A^2 - bx_B^2)\right\} \tag{2.15}$$

The first term vanishes with the limits. Expansion of the remaining integral develops into definitions of the Talmi integral for the indices $p + 1$ and $p + {}^1/_2$. Thus,

$$T_p = \frac{a+b}{a}T_{p+1} - \frac{b}{\sqrt{a}}X_{BA}\frac{\Gamma(p+1)}{\Gamma\left(p+\frac{3}{2}\right)}T_{p+(1/2)} \tag{2.16}$$

which is trivially rearranged to

$$T_{p+1} = \frac{a}{a+b}T_p + \frac{\sqrt{as}}{a+b}X_{BA}\frac{\Gamma(p+1)}{\Gamma\left(p+\frac{3}{2}\right)}T_{p+(1/2)} \tag{2.17}$$

One needs only T_0 and $T_{1/2}$ to start the recurrence relation. The expression for T_0 is

$$T_0 = \sqrt{\frac{a}{a+b}}\exp\left(-\frac{ab}{a+b}X_{BA}^2\right) \tag{2.18}$$

and

$$T_{1/2} = \frac{\sqrt{\pi}b}{a+b}\sqrt{a}X_{BA}T_0 \tag{2.19}$$

Note that if $T_{-|p|} = 0$ for all p, then only T_0 is required to start the recursion as $T_{1/2}$ and all higher half-integer T-quantities are automatically defined; the recursion begins with $p = -1/2$ and the explicit expression for T_0, eq 2.18.

2.4. Matrix Elements for Bond—Bond Terms in the Potential. Matrix elements of the 2-bond many-body terms in the potential are particularly simple to evaluate in the case that the potential is represented as a series in Gaussian basis functions. The Gaussian function contracts to

$$e^{-\lambda b_1 r_1^2 - \mu b_2 r_2^2} = \exp\left(-\frac{\lambda b_1\,\mu b_2}{\lambda b_1 + \mu b_2}r_{CN}^2\right)\exp(-(\lambda b_1 + \mu b_2)r_P^2) \tag{2.20}$$

with

$$\mathbf{r}_P = \mathbf{r}_H - \frac{\lambda b_1\mathbf{r}_C + \mu b_2\mathbf{r}_N}{\lambda b_1 + \mu b_2} \tag{2.21}$$

Thus, for the x-component of the appropriate Talmi integral one finds

$$T_P\{e^{-\lambda b_1 x_1^2 - \mu b_2 x_2^2}\} = \exp\left(-\frac{\lambda b_1\,\mu b_2}{\lambda b_1 + \mu b_2}x_{CN}^2\right)T_p\{e^{-(\lambda b_1 + \mu b_2)x_P^2}\} \tag{2.22}$$

Note, $b \rightarrow \lambda b_1 + \mu b_2$ and B → P in the definition of the Talmi integral, eq 2.11. It is worth noting that the manipulations indicated are general and are not restricted to the example of HCN. If one makes use of multiple points of reference for the wave function basis set, it is still possible to reduce reasonably complicated individual matrix elements to simpler forms. Thus, a relatively small collection of integral subroutines suffices for the entire analysis.

3. Example: HCN

HCN is both a good example and a difficult one to use to test any scheme of analysis that attempts to handle vibrational anharmonic character. The following paragraphs deal, first, with the fitting of the Gaussian model potential, eq 1.1, to an ab initio-generated potential energy surface. Next, a straightforward quantum mechanical analysis of the motion of the hydrogen atom in the field of the fixed atoms C and N is given. Finally, the Discussion suggests some reasonable directions for further work. In particular, drawing a parallel to the molecular electronic problem[2] and the development of modern techniques to handle such systems, a similar approach should, in time, yield practical analyses of the dynamics of hydrogen in a number of settings. To be useful, however, it is necessary that some generally applicable entities be developed: i.e., basis sets for light atoms and small molecular fragments in various environments with stable, optimized sets of orbital exponents much as is the case with Slater functions[17] and the large collection of Gaussian basis functions that are available for modern electronic state calculations.[18,19]

The fitting of HCN to a Gaussian model potential was also considered in a previous paper.[7] There the potential was essentially the same as eq 1.1, but the manipulation was slightly different. Moreover, the potential of ref 7 was fit to data derived from the Murrell et al.[20] potential for HCN.

The potential energy surface for HCN was generated with the Gaussian 03 suite of quantum chemical programs[18] at the MP2 level of approximation using the 6-31G basis set. For the whole molecule, including hydrogen isocyanide, HCN $\rightleftharpoons$ CNH, 3456 points were generated in the *xy*-plane to sample the positions of equilibrium as well as the transition state. The subsequent fitting of this surface to the model potential function yielded a less-than-impressive minimum root mean square error of 150 cm^{-1}, a result that probably reflects more a limited sample point density than the intrinsic accuracy of the fitting function. On the other hand, fitting the model potential only to the species HCN with 1728 points yielded an ultimate root mean square error of 7.3 cm^{-1}. The subsequent analysis of local anharmonicity was carried out using a Gaussian potential fit to this smaller, local set of points. As will be seen, the anharmonic analysis is faithful to the model potential that, in turn, is faithful to the potential energy surface generated from the ab initio quantum chemical routine.

Harmonic-limit frequencies at single optimum equilibrium configurations were also found at the MP2, MP4, and CCSD levels of approximation. In all cases, agreement with experimental frequencies[21] was not as good as one would like, but this difference belongs to the quantum chemical program, not the Gaussian model potential, eq 1.1. Nevertheless, for the purpose of illustration, the subsequent analysis makes use of the potential surface obtained. The results of the ab initio calculations using Gaussian 03 are presented in Table 1.

The fitting of the model potential to the ab initio H-potential energy surface data employed both the Levenberg−Marquardt nonlinear least squares routine and a straight linear least-squares analysis.[22] The Levenberg−Marquardt routine, available in the *Numerical Recipes* package,[22] was modified by replacing the Gaussian elimination routine by a singular value decomposition. The use of large basis sets of simple Gaussian functions seems to lead to instability about pivot points that cause the Gaussian elimination routine to crash due to accidental degeneracies. Although the Levenberg−Marquardt routine can, in principle, also handle linear least squares components in a model potential, it was found that the use of a separate singular value decomposition−least-squares fit, after the initial application of the Levenberg−Marquardt method, yielded much better results. Several separate runs of the least-squares routine eventually resulted in a stable minimum root mean square error with no appreciable further improvement or change in the set of coefficients. In general, modeling potential energy functions with Gaussian basis functions seems to be slightly more temperamental than with other kinds of functions, e.g., basis sets of Morse functions of the kind $y(r) = 1 - \exp[-a(r - r_0)]$.[34]

TABLE 1: Summary of Gaussian 03[17] Calculations

	Optimization (Bond Distances)		
	R_{HC} [Å]	R_{CN} [Å]	
MP2	1.0706	1.1985	
MP4	1.0749	1.1941	
CCSD	1.0736	1.1817	
	Harmonic Frequencies (cm^{-1})		
MP2	681.7 × 2	1907.6	3475.8
MP4	660.2 × 2	1932.3	3426.7
CCSD	689.2 × 2	2075.3	3441.6
expt[20]	727.0 × 2	2129.1	3442.3
	Energy Scan (1,728 points) in the Half-Space		
R_{HC}	1.0 Å → 1.364 Å		
R_{CN}	0.8 Å → 1.296 Å		
Θ_{HCN}	180° → 125°		

Quantum mechanical calculations were carried out using a basis set constructed as a product of three one-dimensional Cartesian basis functions referred to the point of equilibrium for H as the coordinate origin. Thus, the argument of the wave function was $x_{\mathrm{H}} - x_{\mathrm{H}}^0$ with similar terms for the other Cartesian coordinates. The axis of the molecule was chosen to be collinear with the *x*-Cartesian axis. The motion of hydrogen predominately along the *x*-axis therefore corresponded to the H−CN linear stretch. Motions of H in the *xy*,*xz*-planes corresponded to the H−CN angle bend modes. The state function was

$$\Psi(\mathbf{r}) = \sum_{\mathbf{n}} C_{\mathbf{n}} \Phi_{\mathbf{n}}(\boldsymbol{r}) \tag{3.1}$$

where $\mathbf{n} = (n_x, n_y, n_z)$ and

$$\Phi_{\mathbf{n}}(\mathbf{r}) = \prod_{q=x,y,z} \phi_{n_q}(q) \tag{3.2}$$

The maximum quantum number N used for an individual component of the wave function was 9. For the state function, no product of basis functions, $\Phi_{\mathbf{n}}$, exceeded the condition $n_x + n_y + n_z \leq N = 9$. Lower values of N were tried, but the frequency associated primarily with the H−CN stretch seemed reasonably to stabilize with $N = 9$ as the maximum order.

In terms of the component basis functions, each transition from the ground state, $\mathbf{n} = \mathbf{0}$, looked like a mixture of individual basis-transitions along the three Cartesian coordinates. That is, a stretch showed elements of bend, and the converse. This situation, of course, is consistent with the normal mode for an angular bend at (nearly) constant R. The generation of matrix elements and the subsequent variational calculation to determine

TABLE 2: Frequencies, Transition Character, and Transition Moments for the Minimum Stretch Frequency vs Orbital Exponent

orbital exponents (x, y, z): 97.50 Å^{-2}
equivalent harmonic frequencies: 3794.33 cm^{-1}
ground-state energy: 1.23020 eV

0 →	n	ω	$\langle n_x\rangle$	$\langle n_y\rangle$	$\langle n_z\rangle$	μ_x	μ_y	μ_z	μ
0	1	674.50	0.01	0.55	2.65	0.00	0.00	0.52	0.52
0	2	674.50	0.01	2.65	0.55	0.00	0.52	0.00	0.52
0	6	2840.87	0.01	2.55	2.55	0.00	0.08	0.05	0.09
0	7	2840.87	0.01	2.55	2.55	0.00	0.05	0.08	0.09
0	8	3517.60	0.01	2.87	0.84	0.00	0.13	0.03	0.13
0	9	3517.60	0.01	0.84	2.87	0.00	0.03	0.13	0.13
0	10	3820.88	1.00	0.74	0.74	0.14	0.00	0.00	0.14

optimum values of the elements of the vector **C** in eq 3.1 was straightforward to carry out. In addition, two separate orbital exponential quantities a, cf. eq 2.1 were tried, one for the x-coordinate a_x and the other for the y, z-coordinates $a_y = a_z$. In the end, one value of the wave function exponent was used for all the Cartesian bases cf. Table 2 and Figures 1 and 2). Variation of the energy with respect to these quantities yielded a number of local (and sometimes an apparent) global minima. For small values of the orbital exponent, a, the energy minima, however, proved to be unphysical in terms of the frequencies associated with the transitions. The behavior of the HCN system with the variation of the orbital exponents is illustrated in Figures 1 and 2. In the neighborhood of a value of $a_x = 95$ Å^{-2}, the stretch frequency was found to be virtually constant (varying by a few tens of wavenumber) for a much wider range of values for $a_y = a_z$. It was ultimately found that a single value of the orbital exponent a gave reasonable results. Indeed, it was found, as shown in Figure 2, that the system was variationally optimized with respect to the linear stretch frequency.

The analysis of the character of a particular transition was carried out by evaluating two quantities. The first was the effective transition dipole (it needed to be nonzero for a defined difference in energy levels to correspond to a transition), and the second was a transition character analysis that was carried out using the excited-state eigenvector together with the effective quantum number labels taken from the basis functions associated with the eigenvector components. Thus, the effective x-character of a transition is[35]

$$\langle n_x\rangle_I = \sum_{n_x=1,N} n_x C_{I,n_x}{}^2 \tag{3.3}$$

where I is the Ith eigenstate and N is the maximum value of the wave function. Note, the upper value of n_x is limited by the condition $n_x + n_y + n_z \leq N$ and is not necessarily N in a particular sum. There are similar quantities $\langle n_y\rangle_I$ and $\langle n_z\rangle_I$. The triplet of numbers ($\langle n_x\rangle_I$, $\langle n_y\rangle_I$, $\langle n_z\rangle_I$) together with the Cartesian components of the transition dipole gives a reasonable indication of the character of the transition.

Table 2 presents a summary of the transitions found for $a = 97.5$ Å^{-2} associated with the minimum value of the frequency of the linear stretch. Apart from the easily identified lowest angle−bend transition and the linear stretch, there are other transitions essentially involving angular deformations. The doubly degenerate transition at 2841 cm^{-1} appears to have a very small transition probability. From the character of the transition, it involves both the y and z Cartesian components and may be a consequence of the analysis rather than a reflection of reality. The next higher degenerate transition shows a purer character of y or z.

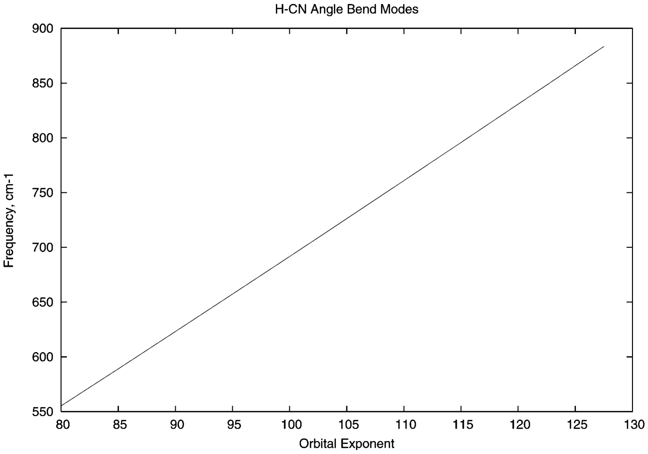

Figure 1. Variation of the H−CN angle bend modes as a function of the original exponent $a_{x(=y,z)}$.

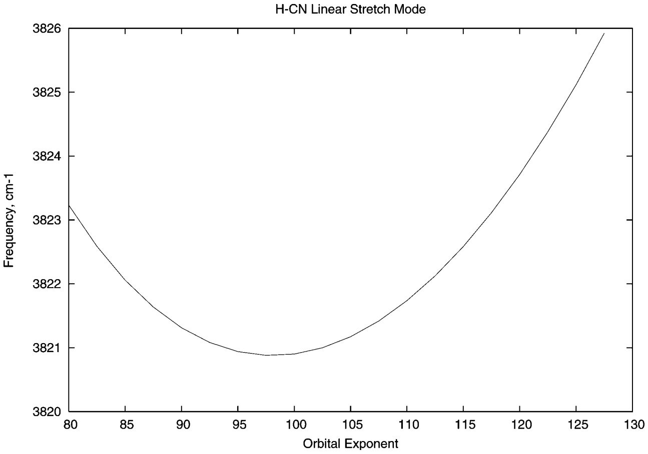

Figure 2. Variation of the H−CN linear stretch mode as a function of the original exponent $a_{x(=y,z)}$.

Although the linear stretch frequency is greater (by about 400 cm^{-1}) than the observed value, there may be a number of explanations for this disagreement. In the earlier work,[7] the Gaussian form of potential was fit to a larger set of points; such a set was easier to generate using the original Murrell potential.[20] It is probably possible to improve these results greatly with a larger and denser set of points for the potential energy surface than was used. The set employed nevertheless illustrates the assertion, namely that it is possible to get reasonable representations of the anharmonic character of the hydrogen atom in particular in a molecular environment that otherwise behaves as a collection of classical oscillators. The angle−bend frequencies obtained with the original Gaussian 03 set of routines[17] also do not agree with experiment. The anharmonic modes analyzed here, however, are more in agreement with the expected value, which should correspond essentially to the harmonic frequency.

Finally, with respect to the illustrative example of HCN, even though there is indeed a minimum in the linear stretch frequency of H against CN, the range of values is quite small. Moreover, the use of a single orbital exponent for both the x and the yz modes is acceptable. This fact has two implications: one, it is a considerable simplification of the analysis only to have to deal with one orbital parameter in the wave function basis set; two, it is much easier to make the transition to spherical oscillator basis functions, if one wishes. All of this suggests, as mentioned earlier, that it ought to be possible to develop a set of orbital exponents for the oscillator basis functions along lines used by Slater years ago[17] to specify adequate basis functions to use for calculations involving the electron(s) in molecules. It seems reasonable to expect that classes of bonds ought to behave essentially the same such that one could construct a set of basis functions associated with the atoms and bonds involved in any arbitrary molecule.

4. Discussion

This treatment of HCN does not include account of the possible, but infrequent (and therefore unlikely because of the high barrier) event of hydrogen tunneling from HCN → CNH. Nevertheless, tunneling in general is an important issue,[23] and the methods presented here can be useful for the treatment of a number of systems in which tunneling is possible. In addition, the analysis adapts to the specific consideration of proton transfer between local minima activated by fluctuations of a polar environment (in a sense analogous to the Marcus electron transfer theory[24]). Although these issues are not treated in this paper, they are the subject of continuing investigation. A brief discussion now follows of the application of this kind of analysis to problems of tunneling.

The simplest type of hydrogen/proton-transfer system has a schematic representation:

$$\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{A} + \mathrm{HB}$$

It is trivial to demonstrate, for example, that the sum of two Morse functions, one for AH and the other for HB yield two minima and a barrier on the line joining A and B.[25−27] The A and B species may be neutral or charged. The AB-distance may also be fixed, although not necessarily rigidly so, when the species are atoms within a larger molecular framework. For free species AH, B, HB, and A in solution, for example, the proton/hydrogen transfer is considered with reference to an instantaneous separation R_{AB}. One eventually needs to average over the ensemble of reactant separations in order to define the reaction rate constant. In any case, it is possible to define points of reference for the proton/hydrogen atom with respect to the two species A and B such that one schematically considers a transition

$$\mathrm{A{-}H{\cdots}B} \rightleftharpoons \mathrm{A{\cdot\cdot}H{\cdot\cdot}B} \rightleftharpoons \mathrm{A{\cdots}H{-}B}$$

for which the A−B distance is fixed. The hydrogen atom migrates between positions of equilibrium in the space between A and B. In the simplest case, there is no intervening atom over or around which the hydrogen atom would need to move in order to make a transition from an initial to a final state.

In the case of HCN ⇌ CNH, however, the space between the two minima for hydrogen is occupied by the CN-species. This is clearly a complicating factor. As the discussion of HCN in the last section pointed out, with the use of Gaussian expansions of the potential energy surface, it is possible to fit an accurate local model potential for the initial and final states without considering the entire molecule. It is also possible to fit a model potential that is referred to intermediate points of expansion in order to be able to evaluate the two-center matrix elements that will arise. The spirit of this approach is generally the same as is used in the density functional theory in which exchange kernels are modeled and fit to Gaussian expansions. The fitting regions are typically those volumes in coordinate space where the influence of the potential is the greatest. The resulting density-functional-theory matrix elements with the (Gaussian) basis functions are also essentially overlap integrals. The evaluation of matrix elements associated with tunneling naturally involves two-center integrals. Such integrals have not been considered in section 3 for the HCN system, but they are discussed in the Appendix for completeness.

In summary, the objective of this paper has been to show that it ought to be possible to evolve analyses of *local* anharmonicity, in particular of hydrogen, in otherwise extended and complicated molecular systems. The nature of the analysis emphasizes the use of *linear combinations* of orthonormal Cartesian harmonic oscillator basis functions together with accurate local representations of the potential energy function built as a power series in very simple Gaussian exponential functions. The essential features of the oscillations of H against (classical) CN for both angle−bend modes and the linear stretch was shown. The agreement with experimental frequencies is (probably) as good as the potential energy surface to which the Gaussian model potential was fit. The transparency of the analysis suggests a straightforward extension to handle the issue of tunneling.

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A. Two-Center Matrix Elements

The body of this paper dealt with the evaluation of matrix elements using wave functions referred to the same coordinate origin; viz.

$$\langle A, m|F(x)|A, n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x_{\mathrm{A}}\, \phi_m(\sqrt{a}x_{\mathrm{A}})\phi_n(\sqrt{a}x_{\mathrm{A}})\, F(x) \quad \text{(A.1)}$$

in which $F(x)$ is an arbitrary function of x. As is well-known from the molecular electronic problem,[28] the simple LCAO method yields two-center matrix elements of the following kind:

$$\langle A, m|F(x)|B,n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x_{\mathrm{A}}\, \phi_m(\sqrt{a}x_{\mathrm{A}})\phi_n(\sqrt{b}x_{\mathrm{B}})\, F(x) \quad \text{(A.2)}$$

These matrix elements arise as a consequence of the use of a linear combination of two primitive basis functions referred to two separate coordinate origins:

$$\Phi_m = A\phi_m(\sqrt{a}x_{\mathrm{A}}) + B\phi_m(\sqrt{b}x_{\mathrm{B}}) \quad \text{(A.3)}$$

Here, A and B are linear coefficients that are determined by the standard variational method of quantum mechanics.[36]

If this approach is applied, for example, to the phenomenon of hydrogen migration within a molecule or between molecules, Cartesian oscillator functions can be used as primitive basis functions for the LCAO approximation, as has been done for HCN in section 3 above. Although the examples of HCN in this paper did not make use of expansions about multiple centers (because tunneling to HNC was not considered), the following discussion of the appropriate manipulations is presented for completeness.

By adopting the Cartesian Gaussian basis functions, one can make use of the Moshinsky-Smirnov transformation[15,16] to condense the product of the two functions into a sum of terms, one of which is a new wave function with reference to a weighted point on the line between the original two points of expansion.[7]

The one-dimensional Talmi transformation operates on the Cartesian harmonic oscillator functions and uses of Smirnov's one-dimensional variant[16] of the Talmi/Moshinsky coefficients. The basis functions are defined by eqs 2.1 and 2.2. The one-dimensional Talmi transformation itself is[16]

$$\phi_{n_1}(\sqrt{a}x_{\mathrm{A}})\phi_{n_2}(\sqrt{b}x_{\mathrm{B}}) = \sum_{N_1,N_2} T(N_1, N_2; n_1, n_2)\phi_{N_1}(\sqrt{a+b}\,X)\phi_{N_2}\left(\left(\frac{ab}{a+b}\right)^{1/2}x\right) \quad (A.4)$$

subject to $n_1 + n_2 = N_1 + N_2$ (conservation of energy) and

$$x = x_{\mathrm{A}} - x_{\mathrm{B}}$$
$$X = \frac{ax_{\mathrm{A}} + bx_{\mathrm{B}}}{a+b} \quad (A.5)$$

The formula

$$T(N_1, N_2; n_1, n_2) = \left(\frac{N_1!N_2!}{n_1!n_2!}\right)^{1/2} \alpha^{(n_2-N_1)/2\beta(n_1-N_1)/2} \times \sum_{i+j=N_1}\binom{n_1}{i}\binom{n_2}{j}\alpha^i(-\beta)^j \quad (A.6)$$

defines the Talmi coefficient $T(N_1, N_2; n_1, n_2)$ with α and β defined as

$$\alpha = 1 - \frac{a}{a+b} \quad (A.7)$$

$$\beta = 1 - \frac{b}{a+b} \quad (A.8)$$

Single species matrix elements depend on the transformation (eq A.4) through the following relationships. Given

$$x_{\mathrm{A}} = x - X_{\mathrm{A}} \qquad x_{\mathrm{B}} = x - X_{\mathrm{B}} \quad (A.9)$$

with X_{A} and X_{B} the locations of the points of expansion of the basis functions, one has

$$X_{\mathrm{BA}} = X_{\mathrm{B}} - X_{\mathrm{A}} \quad (A.10)$$

and

$$x_{\mathrm{P}} = x - \frac{aX_{\mathrm{A}} + bX_{\mathrm{B}}}{a+b} = x - X_{\mathrm{P}} \quad (A.11)$$

Thus, the one-dimensional Talmi transformation is

$$\phi_{n_1}(\sqrt{a}x_{\mathrm{A}})\phi_{n_2}(\sqrt{a}x_{\mathrm{B}}) = \sum_{N_1,N_2} T(N_1, N_2; n_1, n_2) \times \phi_{N_1}(\sqrt{a+b}\,x_{\mathrm{P}})\phi_{N_2}\left(\left(\frac{ab}{a+b}\right)^{1/2}X_{\mathrm{BA}}\right) \quad (A.12)$$

The two-particle matrix elements are not considered here, but they have been discussed elsewhere.[7]

For an arbitrary one-dimensional operator $F(x)$, the use of the Moshinsky-Smirnov transformation in eq A.2 yields[16]

$$\langle A, m|F(x)|B, n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, \phi_m(\sqrt{a}x_{\mathrm{A}})\phi_n(\sqrt{b}x_{\mathrm{B}})\, F(x) = \sum_{M,N} T(MN; mn)\phi_N\left(\sqrt{\frac{ab}{a+b}}X_{\mathrm{BA}}\right) \times \int_{-\infty}^{\infty} \mathrm{d}x_{\mathrm{P}}\, \phi_{\mathrm{M}}(\sqrt{a+b}\,x_{\mathrm{P}})F(x) \quad (A.13)$$

At this point, one can generalize the evaluation of the remaining integral along lines parallel to the BJM analysis of the single center integrals. In particular, using eqs 2.3 and 2.4, one has

$$\langle A, m|F(x)|B, n\rangle = \sum_{M,N} T(MN; mn)\phi_N\left(\sqrt{\frac{ab}{a+b}}X_{\mathrm{BA}}\right) \times \sum_{s=0}^{[m/2]} A_{M,s}(a+b)^{m/2-s}\int_{-\infty}^{\infty} \mathrm{d}x\, x_{\mathrm{P}}^{m-2s} \times \exp\left\{-\frac{1}{2}(a+b){x_{\mathrm{P}}}^2\right\}F(x) = \sum_{M,N} T(MN; mn)\phi_N\left(\sqrt{\frac{ab}{a+b}}X_{\mathrm{BA}}\right)\sum_{\min(p)}^{\max(p)} \mathscr{D}_{M,p}S_p \quad (A.14)$$

The lowercase index $p = m/2 - s$. In eq A.13, $\min(p) = \max(p) - [m/2]$ and $\max(p) = m/2$. The coefficient $\mathscr{D}_{M,p}$ is simply

$$\mathscr{D}_{M,p} = \Gamma(p + {}^1\!/_2)A_{M,M/2-p} \quad (A.15)$$

Finally, the Talmi-like integral S_p is

$$S_p = \frac{\left[\frac{1}{2}(a+b)\right]^{p+(1/2)}}{\Gamma\left(p+\frac{1}{2}\right)}\int_{-\infty}^{\infty} \mathrm{d}x\, x_{\mathrm{P}}^{2p}\exp\left[-\frac{1}{2}(a+b){x_{\mathrm{P}}}^2\right] F(x) \quad (A.16)$$

Note that in the limits as $b \rightarrow a$ and $X_P \rightarrow X_{\mathrm{A}}$ [$X_{\mathrm{BA}} = 0$], then $S_p \rightarrow T_p$, and the BJM coefficient is

$$\lim_{b\rightarrow a}\lim_{X_{\mathrm{BA}}\rightarrow 0}\{\sum_{M,N}\phi_N(X_{\mathrm{BA}})T(MN;mn)\mathscr{D}_{M,p}\} = B(m, n, p) \quad (A.17)$$

Because $\phi_{2N+1}(0) = 0$ [due to $H_{2N+1}(0) = 0$] only even terms in the summation over N survive.

In the case that $F(x) = \exp(-cx_{\mathrm{C}}^2)$, one derives a recurrence relation for S_p that reduces to the associated Talmi integral in the limit $a \rightarrow b$. From the definition of S_p, and integrating by parts, one finds

$$S_{p+1} = \frac{a+b}{a+b+2c}S_p + \frac{\sqrt{2(a+b)c}}{a+b+2c}X_{\mathrm{CP}}\frac{\Gamma(p+1)}{\Gamma\left(p+\frac{3}{2}\right)}S_{p+(1/2)} \quad (A.18)$$

It is clearly the case that

$$\lim_{b\rightarrow a}\lim_{X_{\mathrm{BA}}\rightarrow 0} S_p = T_p \quad (A.19)$$

The quantities S_0 and $S_{1/2}$ are easily found. The preceding establishes a consistent treatment of integrals for the operator $F(x) = \mathrm{e}^{-c{x_c}^2}$.

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(29) It sometimes makes sense to use the do loop construction, e.g., $i = 1, 3$ familiar from Fortran, to express the summation limits.

(30) BJM coefficients are implicit in a number of treatments,[10−16] but they are explicitly derived here. They are essential to the analyses considered in this work.

(31) Note that the Brody−Jacob−Moshinsky[8] coefficients are unchanged if one expresses the Talmi integral only in dimensionless coordinates $\bar{x} = \sqrt{a}x$ with $a = m\omega/\hbar$.

(32) The coordinates of the individual species all are referred to a laboratory coordinate origin. Where confusion is not likely, the H subscript on x_H will be dropped.

(33) See ref 7 for an alternative expression that does not, however, make use of the 1D BJM analysis.

(34) Unpublished results.

(35) This is the expectation value of the number operator $N_{op} = \alpha^{\dagger}\alpha$ where $\alpha^{\dagger}$ and α are the creation and annihilation operators respectively.

(36) As discussed in ref 7, the general treatment of (hydrogenic) anharmonicity under the assumptions of the self-consistent-field (viz., Hartree) approach also yields three- and four-center or higher matrix elements. The appearance of the simpler two-center matrix elements is a consequence of the use of a potential energy function with, at most, pair interactions.