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## A R T I C L E S

# Bound State Potential Energy Surface Construction: Ab Initio Zero-Point Energies and Vibrationally Averaged Rotational Constants

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***Abstract:*** Collins' method of interpolating a potential energy surface (PES) from quantum chemical calculations for reactive systems (Jordan, M. J. T.; Thompson, K. C.; Collins, M. A. *J. Chem. Phys.* **1995**, *102*, 5647. Thompson, K. C.; Jordan, M. J. T.; Collins, M. A. *J. Chem. Phys.* **1998**, *108*, 8302. Bettens, R. P. A.; Collins, M. A. *J. Chem. Phys.* **1999**, *111*, 816) has been applied to a bound state problem. The interpolation method has been combined for the first time with quantum diffusion Monte Carlo calculations to obtain an accurate ground state zero-point energy, the vibrationally average rotational constants, and the vibrationally averaged internal coordinates. In particular, the system studied was fluoromethane using a composite method approximating the QCISD(T)/6-311++G(2df,2p) level of theory. The approach adopted in this work (a) is fully automated, (b) is fully ab initio, (c) includes all nine nuclear degrees of freedom, (d) requires no assumption of the functional form of the PES, (e) possesses the full symmetry of the system, (f) does not involve fitting any parameters of any kind, and (g) is generally applicable to any system amenable to quantum chemical calculations and Collins' interpolation method. The calculated zero-point energy agrees to within 0.2% of its current best estimate. $A_0$ and $B_0$ are within 0.9 and 0.3%, respectively, of experiment.

Molecules in their lowest energy state still possess zero-point vibrational energy. As a consequence, the long-time properties of molecules, which depend on structure, are subject to vibrational averaging. To accurately predict experimental rotational constants, this vibrational averaging must be taken into account. The problem is further compounded if one assumes harmonic vibrations and then corrects the predicted equilibrium rotational constants, regardless of their accuracy, for harmonic vibrational averaging. Perturbation theory indicates that the harmonic corrections to the $r_e$ (equilibrium structure) rotational constants are *always positive*, whereas the observed rotational constants are almost always *smaller* than the $r_e$ constants.[2] The reason for this lies in the anharmonicity of the potential − its effects must be taken into account to accurately predict rotational constants. This can sometimes be achieved by use of perturbation theory, but for systems involving large amplitude motion or possessing highly anharmonic vibrations, such a treatment is inadequate. Furthermore, zero-point vibrational energies are always predicted to be too large under the assumption of harmonic vibrations. For accurate predictions of this quantity, which are required when comparing the energies of different molecules or complexes, anharmonic effects must be considered. A general, widely applicable method is therefore sought that can accurately predict the zero-point energy and observable

rotational constants of molecules and weakly bound complexes. Such a method is described in this work, with specific application to a the semirigid molecule, fluoromethane. The following paragraphs introduce the method adopted in this work.

The quantum diffusion Monte Carlo[3] technique (DMC) is now a fairly well-developed method for solving the Schrodinger equation for the ground state. Included among the areas of application of this method is the solution to the nuclear vibrational Schrodinger equation. The method can also be applied, with more difficulty, to excited vibrational states (see ref 4 and references therein). DMC is capable of treating large numbers of degrees of freedom, which is its advantage over the more traditional variational methods. For example, the DMC method has been applied to the 30 intermolecular degrees of freedom of the water hexamer[5] and 142 and 452 torsions of biomolecular systems.[6]

However, for accurate results, the DMC method requires an accurate potential energy surface (PES). Collins' PES construction method[1] is an intuition free means of building a PES based on the quantities of interest. The method requires the energy, gradient, and second derivative of the potential with respect to internal coordinates at importance sampled locations on the PES. This minimizes the number of data points required to accurately characterize the surface, thus enabling correspondingly higher

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level calculations to be performed for a given CPU time budget. The data on the potential are obtained from ab initio calculations. An interpolation and/or extrapolation is then made from the existing data to any location on the PES. It is important to realize that the method is fully automated and does not require any least-squares fitting. An alternative approach is to calculate the ab initio energies on the fly as the DMC simulation proceeds.[7] However, this approach is only feasible for low levels of ab initio theory and for small molecules treated with fewer than the full degrees of nuclear freedom.

Collins' PES construction method has recently been successfully combined with ab initio calculations and quantum reactive scattering code for the reaction between $H_2O$ + H.[8] The method has also been applied to numerous reactions, using classical trajectories rather than quantum reactive scattering.[9] However, there is no reason thatCollins' PES construction method cannot be applied to bound systems and, in fact, has been in Cartesian coordinates for a linear four atom system (acetylene) using a very approximate variational method to solve the nuclear vibrational Hamiltonian.[10] In this work, we combine, for the first time, the three powerful "first principal" methods: (a) quantum diffusion Monte Carlo, (b) quantum chemical ab initio calculations, and (c) Collins' PES construction method in internal coordinates. This new combined method is applied to an experimentally well-studied five atom system, $FCH_3$. Fluoromethane therefore serves as an excellent test case, being already a nine-dimensional system, for the combined method described here. In this work, we calculate, from first principals, the zero-point energy, vibrationally averaged rotational constants, and internal coordinates of $F^{12}CH_3$ and some isotopomers and compare them with experiment where available.

In the following section, we describe the computational method, followed by a discussion and presentation of the results. In the final section, we present our conclusions.

## Computational Method

The Collins interpolated PES method has already been described elsewhere,[1] so only a very brief summary of the method will be given here. The PES is represented as a weighted sum of Taylor series expansions, truncated after second order, about importance sampled configurations in inverse interatomic distance space. That is

$$V(\mathbf{R}) = \sum_{i=1}^{M} w_i(\mathbf{Z})T_i(\mathbf{Z}) \tag{1}$$

where the sum is taken over all $M = N \times G$ configurations. Here, $N$ is the number of unique configurations, given by the vector of interatomic distances, $\mathbf{R}$, or inverse distances, $\mathbf{Z}$, about which each Taylor series, $T_i$, is expanded, and $G$ is the order of the permutation symmetry group for the system. For $FCH_3$, $G = 6$. Each Taylor series requires the energy, gradient, and second derivative of the potential, which are determined from quantum chemical calculations. $w_i$ is the

**Table 1.** Equilibrium and Vibrationally Averaged Structure of $FCH_3$

| parameter | MP2/6-31G(d) | composite[a] | QCISD(T)/ cc-pVQZ | $r_v$ |
|---|---|---|---|---|
| $r_{CF}$/Å | 1.3919 | 1.3869 | 1.3799 | 1.389(2) |
| $r_{CH}$/Å | 1.0920 | 1.0897 | 1.0864 | 1.110(1) |
| ∠FCH/deg | 109.1073 | 108.7511 | 108.9490 | 108.8(1) |

[a] As calculated from $E$[MP2/6-311++G(2df,2p)] + $E$[QCISD(T)/6-311G(d,p)] − $E$[MP2/6-311G(d,p)].

weight given to Taylor series $T_i$, the parameters in which are determined self-consistently from the quantum chemical data already obtained from the potential, that is, from the $T_j$, $j \neq i$. Note that this method does not involve any fitting of parameters to any assumed functional form. The PES passes exactly through all the ab initio data points.

The quantum chemical calculations were performed at a composite level of theory that approximates the QCISD(T)/6-311++G(2df,2p) level. This was achieved through three independent, lower level, calculations that are analogous to the approach adopted in the G$n$MP2 methods of Pople et al.[11] Here

$$E[\text{QCISD(T)/6-311++G(2df,2p)}] \approx$$
$$E[\text{MP2/6-311G(d,p)}] + \Delta_{basis} + \Delta_{CI} \tag{2}$$

where $\Delta_{basis} = E$[MP2/6-311++G(2df,2p)] − $E$[MP2/6-311G(d,p)], and $\Delta_{CI} = E$[QCISD(T)/6-311G(d, p)] − $E$[MP2/6-311G(d,p)]. All calculations were performed using the Gaussian 98 revision A.6 suite of programs.[12]

Collins' interpolation method requires the energy, first, and second derivatives of the potential. This is available analytically for the MP2 calculations in eq 2, but derivatives of the potential must be obtained numerically at the QCISD(T) level. Central differences were used to obtain the latter quantities.

In the standard Collins' interpolation method,[1] an initial PES is generated from reactants to products for the reaction under study. Here it is appropriate to choose initial configurations that approximately reflect the ground state vibrational wave function. Thus, the configurations for the initial data set were generated by taking one small step to either side of the equilibrium configuration (see Table 1), obtained at the MP2/6-31G(d) level of theory, along each normal coordinate. This resulted in a total of 16 unique configurations, including the MP2/6-31G(d) equilibrium configuration and removing identical configurations. The composite energies, gradients, and seconds were then calculated at these configurations, and the resulting PES was used to determine the equilibrium geometry at the composite level of theory (see Table 1). This configuration was also added to the PES to finally obtain the initial 17 point PES.

The algorithm used for growing the PES was as follows. (1) A quantum diffusion Monte Carlo (DMC) calculation (discrete weighting method) was performed on the current PES. One thousand replicas were used, starting at the equilibrium configuration, with a step size of 5 au and diffusing for 10 000 steps. The, now approximate, 1000 configura-

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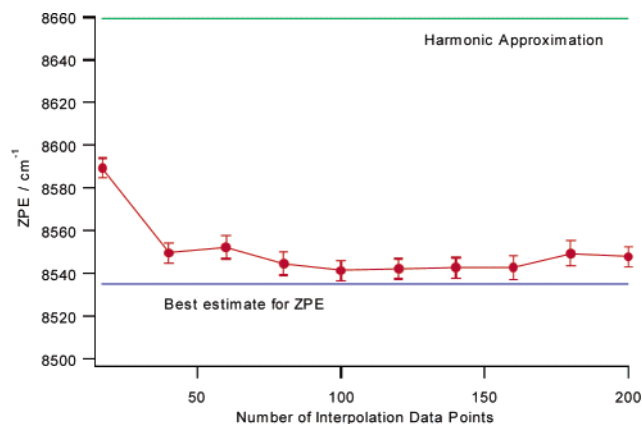
**Figure 1.** The zero-point vibrational energy (ZPE) of $F^{12}CH_3$ as calculated in this work (joined lines with error bars) as a function of interpolation data set size. The error bars indicate twice the standard deviation of the calculated ZPE via the diffusion Monte Carlo method. The current best estimate for the ZPE[15] and the ZPE calculated under the harmonic approximation at the composite level are also indicated.
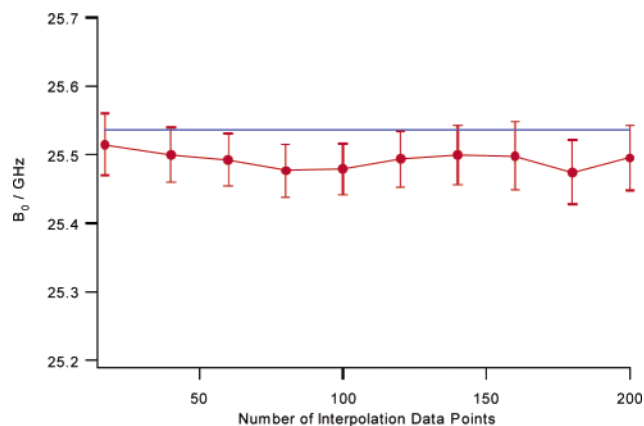
tions were written to disk at step 6000, and every 1000 steps thereafter. (2) The file containing the five samples of the wave function was read. After removing identical configurations, a specific configuration was chosen from this file using alternatively the h-weight method and the RMS method.[1] (3) An ab initio calculation of the energy, first, and second derivatives at the chosen configuration was performed and added to the current PES, before returning back to step 1 above.

Convergence of the PES was checked by performing 70 DMC (discrete weighting) calculations every 25 configurations added to the PES. One thousand replicas were used, starting at the equilibrium configuration, with a step size of 2 au and diffusing for 20 000 steps. The ground state energy, that is, zero-point energy or ZPE, was averaged over the last 10 000 steps in each DMC run. The final ground state energy was given by the mean of the 70 ground state energies with the estimated error being given by $2\sigma/\sqrt{N}$, where $N = 70$, and $\sigma$ is the standard deviation of the 70 energies.

The vibrationally averaged rotational constants and the vibrationally averaged internal coordinates were obtained using the method of descendant weights, which is well described in ref 13. Descendants were followed after 10 000 steps for 2000 steps, with a new set of descendants being followed starting every 200 steps. Thus, after the initial 12 000 steps, 10 sets of descendants were followed simultaneously. The calculated rotational constants and internal coordinates were averaged over the total number of sets of descendants accumulated. To obtain an improved estimate of these quantities, a separate geometry optimization was performed at the QCISD(T)/cc-pVQZ level, and the results (Table 1) were utilized for the $r_e$ structure. That is, displacements away from the composite level $r_e$ structure calculated during the DMC run were applied to the $r_e$ structure at the QCISD(T)/cc-pVQZ level. Note that permutation symmetry was utilized in these calculations. The rotational constants were calculated for each replica by rotating into the Eckart axes[14] and averaging over all permutations the resultant inverted moment of inertia tensor. The final set of rotational constants and internal coordinates was obtained by averaging them over the 70 DMC runs, with the estimated error being given by $2\sigma/\sqrt{N}$, where $N = 70$, and $\sigma$ is the standard deviation of a rotational constant or internal coordinate from the 70 runs.

## Results and Discussion

Figure 1 shows the calculated ZPE for the main species $F^{12}CH_3$ as a function of the number of points in the interpolated

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**Figure 2.** $B_0$ of $F^{12}CH_3$ as calculated in this work (joined lines with error bars) as a function of interpolation data set size. The error bars indicate twice the standard deviation of the calculated $B_0$ via the diffusion Monte Carlo method. The experimental value for $B_0$ is indicated as a horizontal line.
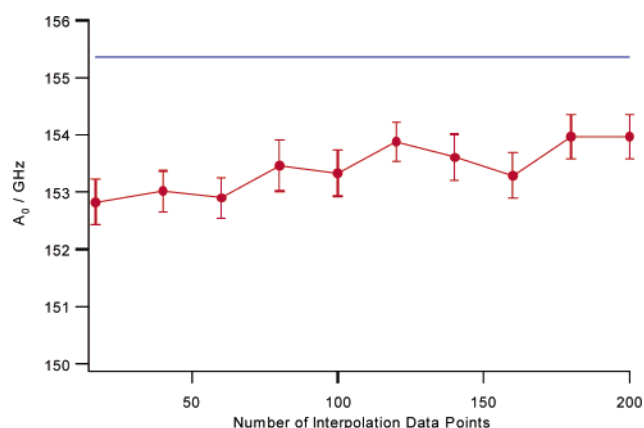


**Figure 3.** $A_0$ of $F^{12}CH_3$ as calculated in this work (joined lines with error bars) as a function of interpolation data set size. The error bars indicate twice the standard deviation of the calculated $A_0$ via the diffusion Monte Carlo method. The experimental value for $A_0$ is indicated as a horizontal line.

PES. It is clear from this figure that the ZPE has converged to the final result when the interpolation data file contains around 100 points. Also indicated on this figure is the ZPE obtained using the harmonic approximation (at the composite level), and the previous best estimate for the ZPE.[15] The latter was obtained from the results of a variational calculation. This calculation was performed on a potential derived by adjusting parameters from an anharmonic force field to reproduce experimental fundamental frequencies. While the calculation presented in the current work is possibly more accurate than the previous results in regard to the ZPE, the previous work involves fitting a potential to experiment, which tends to hide errors in the assumed model of ref 15. In the present work, the final calculated ZPE was $8548 \pm 5$ cm$^{-1}$ and is within 0.2% of the previous estimate, 8535 cm$^{-1}$, from ref 15.

Figures 2 and 3 show the calculated and experimental $B_0$ and $A_0$ rotational constants, respectively, for the main species $F^{12}CH_3$. Figure 2 indicates that the value of $B_0$ is hardly changed as the data set increases in size, while Figure 3 indicates a slight increase in the calculated value of $A_0$ as the data set size increases.

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**Table 2.** Calculated and Experimental Rotational Constants (GHz) for FCH$_3$

| rotational constant | experiment[a] | theory |
|---|---|---|
| $A_0$ (F$^{12}$CH$_3$) | 155.353 | $153.97 \pm 0.39$ |
| $B_0$ (F$^{12}$CH$_3$) | 25.536 | $25.50 \pm 0.05$ |
| $A_0$ (F$^{12}$CD$_3$) | 78.040 | $77.46 \pm 0.16$ |
| $B_0$ (F$^{12}$CD$_3$) | 20.450 | $20.40 \pm 0.02$ |
| $A_0$ (F$^{13}$CH$_3$) | | $153.49 \pm 0.27$[b] |
| $B_0$ (F$^{13}$CH$_3$) | 24.862 | $24.79 \pm 0.04$[b] |

[a] Errors are less than the last decimal place shown. Experimental data are taken from ref 16 and references therein. [b] Averaged over 100, rather than 70, DMC runs.

The vibrationally averaged rotational constants for the isotopomers F$^{12}$CD$_3$ and F$^{13}$CH$_3$ were also calculated and compared with experiment. The results are indicated in Table 2 and were calculated using the 200 point interpolation data set. The experimental value for $A_0$ is not available for F$^{13}$CH$_3$, but agreement between theory and experiment is within 0.8, 0.3, and 0.3% for $A_0$ F$^{12}$CD$_3$, $B_0$ F$^{12}$CD$_3$, and $B_0$ F$^{13}$CH$_3$, respectively.

There are several possible sources of error between the calculated and experimental rotational constants. One is the accuracy of the interpolated potential. A second is the accuracy of the level of ab initio theory used. A third is the systematic errors in the DMC method, and a fourth is whether the experimental constants are *exactly* the same as the vibrational averages of the inverted moment of inertia tensor in the Eckart axis system.

It is difficult to precisely assess the relative magnitudes of each of these sources of error, but several observations can be made. First, previous experience in interpolating PES for reactive systems indicates that interpolation errors can be expected to be as low as 0.4% of the energy range encountered in the problem. Here we are interpolating over a much smaller region of configuration space, so interpolation errors could easily be as low as 0.1% or lower, which has been achieved in previous work.[17] This corresponds to about 8 cm$^{-1}$ or lower and might be the reason for the difference in the current calculated ZPE and the previous value. The impact of these small errors on the rotational constants is unknown, but it can be seen that the variation of $B_0$ with interpolation data set size is small.

Furthermore, the statistical error in the DMC result for $B_0$ places the calculated value within, or very nearly within, the observed value.

We find here that the vibrational correction to the equilibrium rotational constants is negative, as expected. However, it is noted that the calculated $B_0$ and, more significantly, $A_0$ are both lower than the observed values. It is also noted that there is a slight systematic variation in the calculated equilibrium values of these constants on going from the MP2/6-31G(d) to the composite level and finally to the QCISD(T)/cc-pVQZ values. In each case, the constants increase. It is therefore possible that an even higher level of ab initio theory may bring the calculated rotational constants into still better agreement with experiment.

Finally, the observed rotational constants include some effects due to rotation. Perturbation theory predicts three main contributions to the vibrationally averaged constants:[2] (i) a harmonic contribution, (ii) an anharmonic contribution, and (iii) a Coriolis contribution. The former two are taken account of in the present work, but the latter has been neglected. While this effect is usually small, it is a possible source of error that could contribute somewhat to the difference between the experimental and calculated $A_0$ value.

## Conclusion

A method has been provided in which a first principal calculation is shown to be possible for the zero-point energy and vibrationally averaged rotational constants for a five atom system, specifically FCH$_3$. It was shown that an accuracy of 0.9% in the $A_0$ rotational constant is possible, and better than 0.2% for the ZPE and 0.3% for the $B_0$ rotational constant. The method can, in principle, be applied to much larger systems. The method (a) is completely automated, (b) is fully ab initio, (c) includes all nuclear degrees of freedom, (d) requires no assumptions regarding the functional form of the PES, (e) possesses the full symmetry of the system, (f) does not involve fitting any parameters of any kind, and (g) is generally applicable to any system amenable to quantum chemical calculations and Collins' interpolation method. Work is currently in progress to obtain the fundamental frequencies of vibration.

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