

Molecular Geometries and Harmonic Frequencies from the Parametric Two-Electron Reduced Density Matrix Method with Application to the HCN \leftrightarrow HNC Isomerization[†]

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Energies, geometries, and harmonic frequencies of the chemical species in the HCN \leftrightarrow HNC isomerization including the transition state are computed with the parametric variational two-electron reduced density matrix (2-RDM) method. The parametric 2-RDM method parametrizes the 2-RDM with single- and double-excitation coefficients to be both size-consistent and nearly N -representable [DePrince, A. E., III; Mazziotti, D. A. *Phys. Rev. A* 2007, 73, 042501.]. With the inclusion of the zero-point energies of both species, the energy of HNC relative to HCN in a polarized valence triple- ζ basis set is 14.2 kcal/mol, which agrees with the experimental value of 14.8 ± 2 kcal/mol. The present calculations provide the first assessment of the method for computing harmonic frequencies from a molecular geometry optimization. Bond lengths, angles, and harmonic frequencies are also computed for HF, CO, and H₂O.

I. Introduction

The presence of only two-body interactions in many-electron systems suggests that the two-electron reduced density matrix (2-RDM) rather than the wave function might be employed as the fundamental variable in quantum chemistry.¹ For 50 years, however, the direct calculation of the 2-RDM was hindered because the 2-RDM must be constrained to represent an N -particle system where these constraints are known as N -representability conditions.^{2,3} Recently, methods for computing the 2-RDM without the many-electron wave function have been developed, including the nonvariational methods that solve the anti-Hermitian contracted Schrödinger equation (ACSE) for the 2-RDM^{4–6} and the variational 2-RDM methods that minimize the energy with respect to the 2-RDM constrained by necessary N -representability conditions.⁷ The authors, extending work by Kollmar,⁸ have parametrized the 2-RDM in the variational 2-RDM methods with single- and double-excitation coefficients from single–double configuration interaction (CISD) to produce a technique that we call the parametric variational 2-RDM method.^{8–10} The approach agrees with full configuration interaction for two-electron atoms and molecules, scales linearly with system size, and yields 2-RDMs that nearly satisfy the D, Q, and G conditions for N -representability.^{1–3,11}

The isomerization reaction HCN \leftrightarrow HNC, which is important in interstellar chemistry,¹² has been of significant theoretical and experimental interest for more than 30 years. While the reaction is conceptually simple, a unimolecular isomerization involving only the migration of a single hydrogen atom, the energy difference between HCN and HNC was unclear from experimental measurements in the early 1980s.^{13–16} Blackman et al.¹³ showed that the energy of HNC relative to that of HCN must be at least 10.8 kcal/mol, while Maricq et al.¹⁵ concluded that the energy difference must be more than 17.2 kcal/mol, and Maki and Sams¹⁴ predicted a relative energy of 10.3 kcal/mol. Pau and Hehre¹⁶ employed ion cyclotron double-resonance spectroscopy to show that HCN is more stable than HNC by

14.8 ± 2 kcal/mol. This latter value is consistent with both early¹⁷ and more recent theoretical calculations.^{18,19} Aside from these initial experimental discrepancies, “semiempirical” potential energy surfaces such as those computed by Murrell et al.²⁰ were later shown, by comparison with high-level ab initio calculations, to have serious deficiencies, most notably in the activation energies. The Murrell surface gives a barrier to the HNC \rightarrow HCN isomerization of 34.8 kcal/mol, while the coupled cluster methods predict a barrier that is roughly 10 kcal/mol larger.¹⁸

Theoretical studies of the HCN \leftrightarrow HNC isomerization have been largely performed within the framework of traditional wave function methods^{21,22} such as Moller–Plesset (MP) perturbation theory, configuration interaction (CI), and coupled cluster methods, with the latter methods giving accurate geometries, relative energetics, and spectroscopic constants^{18,19} at a reasonable computational cost. In this paper, the parametric 2-RDM method is applied to computing the energies, geometries, and harmonic frequencies of the chemical species in the HCN \leftrightarrow HNC isomerization including the transition state. Calculations are performed in the correlation-consistent valence triple- ζ basis set (cc-pVTZ).²³ After correction for the zero-point energies, the energy of HCN relative to that of HNC from the 2-RDM method is 14.2 kcal/mol, which agrees with the experimental value of 14.8 ± 2 kcal/mol by Pau and Hehre.¹⁶ These calculations provide the first assessment of the method for computing harmonic frequencies from a molecular geometry optimization. Bond lengths, angles, and harmonic frequencies are also computed for HF, CO, and H₂O.

II. Theory Section

A. Parametric Approach to Variational 2-RDM Theory.

We briefly review the variational parametric 2-RDM functional, as the details of its implementation are described elsewhere.^{8–10} Consider the CISD wave function with a single Hartree–Fock (HF) reference function $|\Psi_0\rangle$

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$$|\Psi\rangle = b_0|\Psi_0\rangle + \sum_a b_i^a |\Psi_i^a\rangle + \sum_{a<b} b_{ij}^{ab} |\Psi_{ij}^{ab}\rangle \quad (1)$$

where i and j are occupied spin orbitals, a and b are unoccupied spin orbitals, b_i^a and b_{ij}^{ab} are the single- and double-excitation coefficients, and $|\Psi_i^a\rangle$ and $|\Psi_{ij}^{ab}\rangle$ are singly and doubly excited determinants. The excitation coefficients are normalized to unity

$$|b_0|^2 = 1 - \sum_a |b_i^a|^2 - \sum_{a<b} |b_{ij}^{ab}|^2 \quad (2)$$

To regain size-consistency, we introduce an eight-index topological factor, f , into the associated energy functional¹⁰

$$E = E_0 + 2 \sum_{\substack{a<b \\ i<j}} \left(1 - \sum_{\substack{c \\ k}} |b_k^c|^2 f_{ijkl}^{abcc} - \sum_{\substack{c<d \\ k<l}} |b_{kl}^{cd}|^2 f_{ijkl}^{abcd} \right)^{1/2} b_{ij}^{ab} \langle \Psi_0 | \hat{H} | \Psi_{ij}^{ab} \rangle + 2 \sum_a \left(1 - \sum_{\substack{c \\ k}} |b_k^c|^2 f_{iikk}^{aacc} - \sum_{\substack{c<d \\ k<l}} |b_{kl}^{cd}|^2 f_{iikl}^{aacd} \right)^{1/2} b_i^a \langle \Psi_0 | \hat{H} | \Psi_i^a \rangle + \sum_a \sum_c b_i^a b_k^c \langle \Psi_i^a | \hat{H} - E_0 | \Psi_k^c \rangle + \sum_{\substack{a<b \\ i<j}} \sum_{\substack{c<d \\ k<l}} b_{ij}^{ab} b_{kl}^{cd} \langle \Psi_{ij}^{ab} | \hat{H} - E_0 | \Psi_{kl}^{cd} \rangle + 2 \sum_{\substack{a<b \\ i<j}} \sum_c b_{ij}^{ab} b_k^c \langle \Psi_{ij}^{ab} | \hat{H} | \Psi_k^c \rangle \quad (3)$$

where E_0 represents the energy of the HF reference wave function, and the topological factor proposed in ref⁸ is defined as

$$f_{ijkl}^{abcd} = \frac{1}{4}(\delta_{ik} + \delta_{il} + \delta_{jk} + \delta_{jl} + \delta_{ac} + \delta_{ad} + \delta_{bc} + \delta_{bd}) - \frac{1}{16}(\delta_{ik} + \delta_{il} + \delta_{jk} + \delta_{jl})(\delta_{ac} + \delta_{ad} + \delta_{bc} + \delta_{bd}) \quad (4)$$

In evaluating the topological factor, the delta function δ_{ik} is 1 when the spatial components of orbitals i and k are the same and 0 otherwise. Setting all $f_{ijkl}^{abcd} = 1$ produces the CISD solution, while setting all $f_{ijkl}^{abcd} = 0$ yields CEPA-0 with single excitations. Equation 3 is minimized by unconstrained optimization with respect to the set of configuration-interaction-like coefficients, $\{b_i^a, b_{ij}^{ab}\}$.

B. Stationary Point Search. Stationary points are located by the Newton–Raphson (NR) algorithm²⁴ in which the update to the geometry vector y , given in internal coordinates, is defined as

$$\Delta y = -H^{-1}g \quad (5)$$

where H is the Hessian matrix of second derivatives and g is the energy gradient. We compute each component of the gradient by the second-order centered finite-difference formula with a displacement for bond distances and angles of $0.02 a_0$ and 0.02 radians ($\sim 1.15^\circ$), respectively. The off-diagonal elements of the second-derivative matrix were computed by the

first-order finite-difference formula, given in refs 5 and 24, while the diagonal elements were computed by the second-order central-difference formula.²⁵ Each internal coordinate was converged to $<10^{-5}$ with optimal equilibrium structures typically determined within five iterations. Each iteration requires $2n + n(n-1)/2 + 1$ energy evaluations, with n being the number of internal coordinates required to define the geometry of the system uniquely.

The geometry of the HCN \leftrightarrow HNC transition state was determined by the same algorithm. If given an initial geometry close enough to the desired transition state (i.e., one in which the Hessian has one and only one negative eigenvalue), the NR algorithm minimizes along each eigenfunction with a positive eigenvalue and maximizes along the eigenfunction with a negative eigenvalue.²¹ The surface for the isomerization in question is sufficiently simple that a reasonable guess for the transition-state geometry produces a Hessian with only one negative eigenvalue.

III. Applications

A. Computational Details. The parametric variational 2-RDM method was employed to locate optimal equilibrium geometries for HF, CO, and H₂O in the cc-pVQZ basis set²³ according to the NR algorithm outlined in the previous section. Once a stationary point was located, normal-mode frequency analysis by the FG method of Wilson, Decius, and Cross²⁶ was performed. For consistency, the same NR algorithm and frequency analyses were utilized to obtain geometries and frequencies from the CISD, CCSD, and CCSD(T) methods as implemented for single-point energy calculations in the GAMESS electronic structure package.^{27,28} Ground-state energies, geometries, and frequencies were also determined for HCN, HNC, and their transition state (CHN)[‡] in the cc-pVTZ basis set²³ by the parametric 2-RDM method as well as CISD, CCSD, and CCSD(T). In all calculations, core orbitals were frozen, which means that they are restricted to be occupied. One- and two-electron integrals were obtained from the GAMESS²⁷ package. Experimental results were obtained from ref 29. Calculated harmonic frequencies typically overestimate experimental values by as much as 5%;³⁰ this occurs for two reasons, (i) the limitations inherent in finite basis sets and electron-correlation methods and (ii) the effect of anharmonicity on experimentally observed fundamental frequencies. Scaling factors, such those employed by Pulay,³¹ can be employed as corrections, but the harmonic frequencies reported here are unscaled.

B. Results and Discussion. Energies, bond lengths, and frequencies computed for HF, CO, and H₂O in the cc-pVQZ basis set are shown in Table 1 for the CISD, CCSD, CCSD(T), and 2-RDM methods. In general, we observe excellent agreement between CCSD- and 2-RDM-optimized geometries. The 2-RDM and CCSD methods yield bond lengths for CO that differ by at most 0.0012 Å. For each molecule shown, the 2-RDM bond lengths or angles slightly improve upon the results from CCSD relative to CCSD(T) and experiment. The harmonic frequencies from the 2-RDM method are also slightly better than those from CCSD, with one interesting exception where the improvement is more substantial. In the case of H₂O, the frequencies for the asymmetric stretch, here denoted as ω_1 , are predicted by the CCSD, CCSD(T), and 2-RDM methods to be 3988, 3951, and 3968 cm⁻¹. Hence, the asymmetric frequency from the 2-RDM approach, differing from CCSD and CCSD(T) by -20 and $+17$ cm⁻¹, is closer to the value from CCSD(T). In contrast, the frequencies for the symmetric stretch ω_2 and the bending mode ω_3 computed by the CCSD and 2-RDM approaches are within 5 cm⁻¹.

TABLE 1: Ground-State Energies, Optimized Geometries, And Frequencies for H₂O, HF, and CO in the cc-pVQZ Basis Set Presented from the Parametric 2-RDM Method As Well As Several Correlated Wave Function Methods Including CISD, CCSD, and CCSD(T)^a

	method				expt.
	CISD	CCSD	CCSD(T)	2-RDM	
HF					
energy	−100.3554	−100.3654	−100.3732	−100.3657	
r_{HF}	0.9106	0.9138	0.9164	0.9142	0.9168
ω_1	4258	4204	4161	4193	4138
CO					
energy	−113.1447	−113.1694	−113.1879	−113.1725	
r_{CO}	1.1183	1.1245	1.1315	1.1257	1.1283
ω_1	2288	2234	2164	2216	2170
H ₂ O					
energy	−76.3393	−76.3508	−76.3598	−76.3516	
r_{OH}	0.9518	0.9554	0.9580	0.9557	0.9578
a_{HOH}	104.6941	104.3983	104.1142	104.3301	104.4776
ω_1	4044	3988	3951	3968	3756
ω_2	3943	3884	3843	3879	3657
ω_3	1684	1672	1660	1675	1595

^a Energies, bond lengths, and angles are reported in Hartrees, Angstroms, and degrees, while the frequencies of the vibrational normal modes are in cm^{−1}.

TABLE 2: Ground-State Energies, Optimized Geometries, And Frequencies for HCN, HNC, and the Transition State (CHN)[‡] of the Isomerization in a cc-pVTZ Basis Set Presented from the Parametric 2-RDM Method As Well As Several Correlated Wave Function Methods Including CISD, CCSD, and CCSD(T)^a

	method				expt.
	CISD	CCSD	CCSD(T)	2-RDM	
HCN					
r_{HC}	1.0610	1.0649	1.0670	1.0655	1.0640
r_{CN}	1.1450	1.1528	1.1602	1.1535	1.1560
ω_1	3528	3472	3443	3462	3312
ω_2	2244	2175	2111	2169	2089
ω_3	777	742	716	672	712
ΔE^\ddagger	48.9	48.2	47.8	47.3	
$\Delta E^\ddagger + \text{ZPE}$	45.5	44.7	44.4	44.0	
HNC					
r_{HN}	0.9899	0.9941	0.9965	0.9943	0.9862
r_{CN}	1.1621	1.1685	1.1756	1.1697	1.1726
ω_1	3924	3861	3824	3853	3653
ω_2	2160	2108	2045	2095	2029
ω_3	513	494	472	469	477
ΔE^\ddagger	35.2	33.6	32.8	33.0	
$\Delta E^\ddagger + \text{ZPE}$	32.0	30.5	29.7	29.8	
(CHN) ‡					
r_{HC}	1.1649	1.1765	1.1841	1.1826	
r_{CN}	1.1777	1.1870	1.1945	1.1892	
a_{HCN}	74.9543	73.0276	71.9170	72.0602	
ω_1	2754	2676	2630	2653	
ω_2	2127	2051	1992	2030	

^a Bond lengths, angles, and frequencies are reported in Hartrees, Angstroms, and cm^{−1}, while the energy barriers, denoted ΔE^\ddagger , are given in kcal/mole. Zero-point energies (ZPE) account for all three vibrational modes in the equilibrium structures and the two vibrational modes with real frequencies in the transition state.

The isomerization reaction $\text{HCN} \leftrightarrow \text{HNC}$ has been investigated in the cc-pVTZ basis set utilizing the parametric variational 2-RDM approach as well as CISD, CCSD, and CCSD(T). Table 2 presents the optimal bond lengths, angles, and normal frequencies for the three species involved in the isomerization, HCN, HNC, and the transition state (CHN)[‡]. The results from CCSD and CCSD(T) agree with those from earlier coupled-cluster treatments,^{18,19} expect for the fundamental frequencies of Bowman et al.,^{19d} which were obtained from vibrational second-order perturbation theory³³ rather than the harmonic approximation employed here.

For the equilibrium structure of HCN, the 2-RDM results for bond lengths and frequencies are slightly better than CCSD relative to CCSD(T) and experiment, with the exception of the bending frequency of H–C–N. For this bend, the 2-RDM predicts a frequency of 672 cm^{−1}, which is 44 cm^{−1} lower than that predicted by CCSD(T), while the CCSD value is 742 cm^{−1}, 26 cm^{−1} higher than CCSD(T). The energy barriers to the reaction $\text{HCN} \rightarrow \text{HNC}$ predicted by the CISD, CCSD, CCSD(T), and 2-RDM methods are 45.5, 44.7, 44.4, and 44.0 kcal/mol, respectively, where these barriers include corrections for the zero-point energies. The zero-point energies, accounting for

the three vibrational modes of HCN and the two vibrational modes of the transition state with real frequencies, lower the barriers by 3.5, 3.5, 3.4, and 3.3 kcal/mol for each method, respectively. Both of the CCSD and 2-RDM barriers are within 0.4 kcal/mol of the CCSD(T) result.

For the equilibrium structure of HNC, the 2-RDM method slightly improves the bond lengths, angles, and normal frequencies from their CCSD values. The exception, as in the case of HCN, is the bending frequency. The frequencies of the H–N–C bend from CCSD and the 2-RDM method differ from CCSD(T) by 24 and -3 cm^{-1} , respectively. The energy barriers of the reaction $\text{HNC} \rightarrow \text{HCN}$ from the CISD, CCSD, CCSD(T), and 2-RDM methods are 32.0, 30.5, 29.7, and 29.8 kcal/mol with the corrections for the zero-point energies included. The 2-RDM value is within 0.1 kcal/mol of the CCSD(T) value. The ground-state energies of HNC from the CISD, CCSD, CCSD(T), and 2-RDM methods, relative to energies of HCN, are 13.4, 14.3, 14.7, and 14.2 kcal/mol, which agree with the value of 14.8 ± 2 kcal/mol from experiment.¹⁶

Because previous calculations with the parametric variational 2-RDM method indicate that it performs significantly better than CCSD in single-bond dissociation, it may not be surprising that the 2-RDM method produces geometry and normal-mode frequencies for the transition state $(\text{CHN})^\ddagger$ that improve upon CCSD relative to CCSD(T). In both the H–C bond length and the H–C–N angle, the 2-RDM geometry agrees closely with the geometry from CCSD(T). The H–C–N angle is an especially critical coordinate in the isomerization. The CCSD, CCSD(T), and 2-RDM methods predict H–C bond lengths of 1.1765, 1.1841, and 1.1826 Å with the 2-RDM method only -0.0015 Å from CCSD(T). Similarly, these techniques yield H–C–N angles of 73.03, 71.92, and 72.06°, and hence, CCSD gives a H–C–N angle that differs by nearly 1° from the CCSD(T) result, while the 2-RDM and CCSD(T) angles lie within 0.15° of each other. Significant improvement over CCSD is also observed in one of the two real vibrational frequencies of $(\text{CHN})^\ddagger$. The first normal frequency ω_1 lies halfway between the CCSD and CCSD(T) results of 2676 and 2630 cm^{-1} .

IV. Conclusions

In the parametric variational 2-RDM method,^{8–10} the 2-RDM is parametrized with one- and two-electron excitation coefficients for consistency with the Cauchy-Schwartz counterparts of the D, Q, and G conditions for N -representability.^{1–3,11} Because the N -representability of the 2-RDM is approximately enforced by the parametrization, the ground-state electronic energy can be minimized by unconstrained optimization rather than constrained optimization (or semidefinite programming) as in the variational 2-RDM method.^{7,32} Although the parametric variational 2-RDM method does not produce a strict lower bound like the variational 2-RDM method, it is size-consistent and nearly N -representable. Computationally, it has a cost in floating-point operations and storage like that of CISD; timings from the present implementation, which is not fully optimized, are given in ref 10. At equilibrium geometries, the method yields ground-state energies that are slightly better than those from CCSD, while at nonequilibrium geometries, it significantly improves upon the energies from traditional coupled-cluster methods. Details of the method's accuracy at stretched geometries can be found in refs 9 and 10.

In this paper, we have applied the parametric variational 2-RDM method to optimizing molecular geometries and computing harmonic frequencies for the chemical species of the $\text{HCN} \leftrightarrow \text{HNC}$ isomerization as well as the molecules HF, CO,

and H_2O . At local minima on the potential energy surface, the method produces energies, bond lengths, angles, and normal-mode frequencies that are slightly more accurate than those from CCSD. At transition states like $(\text{CHN})^\ddagger$, however, the 2-RDM method yields geometric parameters and normal-mode frequencies that are closer to CCSD(T) than CCSD. Because the molecule is significantly displaced from its equilibrium $C_{\infty v}$ structure in the transition state, the accuracy of the parametric 2-RDM method that is observed at stretched geometries^{9,10} appears in the transition state's energies, optimal geometries, and harmonic frequencies. Future directions of research include the development of analytical rather than numerical geometry optimization and the extension of the method to treat both closed- and open-shell molecules. The parametric 2-RDM method, incorporating N -representability conditions through its parametrization, represents a significant extension of the variational 2-RDM methods with the potential for important applications to the ground-state energies, geometries, and properties of many-electron atoms and molecules.

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