Supporting Information for

Multilevel Approach for Direct VSCF/VCI MULTIMODE Calculations with Applications to Large “Zundel” Cations

Jake A. Tan and Jer-Lai Kuo**

Institute of Atomic and Molecular Sciences, Academia Sinica, No.1 Roosevelt Road, Section 4, Taipei 10617, Taiwan (ROC)

AUTHOR INFORMATION

Corresponding Authors

* E-mails: jaketan@gate.sinica.edu.tw and jlkuo@pub.iams.sinica.edu.tw

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A. Generation of the Gauss-Hermite Quadrature Grid Points

Let $\left\{\phi_n^s\left(Q_s\right)\right\}$ be the set of harmonic oscillator wave functions for the normal coordinate Q_s. For each Q_s, there exists a harmonic frequency ν_s. The explicit form of $\phi_n^s\left(Q_s\right)$ can be written as[1]

$$\phi_n^s\left(Q_s\right)=N_n H_n\left(\alpha_s Q_s\right)\exp\left(\frac{-\alpha_s^2 Q_s^2}{2}\right)$$
$$N_n=\sqrt{\frac{\alpha_s}{2^n n!\sqrt{\pi}}}\,,\qquad \alpha_s=\left(\frac{\omega_s}{\hbar}\right)^{\frac{1}{2}} \tag{S.1}$$

Where ω_s is the angular frequency for normal mode Q_s, and $\hbar$ is the reduced Planck constant. Let $\mathbf{Q_s}$ be the matrix representation of Q_s in the $\left\{\phi_n^s\left(Q_s\right)\right\}$ basis. For this case, the matrix elements $\left(\mathbf{Q_s}\right)_{ij}$ is expressible in closed form.[2]

The diagonal elements are given by

$$\begin{aligned}&\left(\mathbf{Q_s}\right)_{ii}=\left\langle\phi_i^s\left|Q_s\right|\phi_i^s\right\rangle\\&=N_iN_i\int_{-\infty}^{+\infty}H_i^s\left(\alpha_sQ_s\right)Q_sH_i^s\left(\alpha_sQ_s\right)\exp\left(-\alpha_s^2Q_s^2\right)dQ_s\\&=0\end{aligned} \tag{S.2}$$

The product $H_i^s\left(\alpha_s Q_s\right) H_i^s\left(\alpha_s Q_s\right)\, \exp\left(-\alpha_s^2 Q_s^2\right)$ will always be an even function, while Q_s is an odd function. Therefore, the above integrand is odd, and the integral vanishes. Meanwhile, the off-diagonal elements are given by

$$\begin{aligned}\left(\mathbf{Q_s}\right)_{ij} &= \left\langle \phi_i^s \middle| Q_s \middle| \phi_j^s \right\rangle \\ &= N_i N_j \int_{-\infty}^{+\infty} H_i^s\left(\alpha_s Q_s\right) Q_s H_j^s\left(\alpha_s Q_s\right)\, \exp\left(-\alpha_s^2 Q_s^2\right) dQ_s\end{aligned} \tag{S.3}$$

The above integral is simplified thru the use of the following recursion equation.[1]

$$\xi H_j^s\left(\xi\right) = jH_{j-1}^s\left(\xi\right) + \frac{1}{2} H_{j+1}^s\left(\xi\right), \qquad \xi \equiv \alpha_s Q_s \tag{S.4}$$

The integral in Eq (S.3) then becomes,

$$\begin{aligned}\left(\mathbf{Q_s}\right)_{ij} &= \frac{N_i N_j}{\alpha_s^2} \int_{-\infty}^{+\infty} H_i^s\left(\xi\right)\left[jH_{j-1}^s\left(\xi\right) + \frac{1}{2} H_{j+1}^s\left(\xi\right)\right] \exp\left(-\xi^2\right) d\xi \\ &= \frac{N_i N_j}{\alpha_s^2} \left\{ \begin{array}{l} 2j\int_{-\infty}^{+\infty} H_i^s\left(\xi\right) H_{j-1}^s\left(\xi\right)\, \exp\left(-\xi^2\right) d\xi + \\ \frac{1}{2}\int_{-\infty}^{+\infty} H_i^s\left(\xi\right) H_{j+1}^s\left(\xi\right)\, \exp\left(-\xi^2\right) d\xi \end{array} \right\}\end{aligned} \tag{S.5}$$

Recall that for Hermite polynomials, the following orthogonality condition holds.[1]

$$\int_{-\infty}^{+\infty} H_n^s\left(\xi\right) H_m^s\left(\xi\right) \exp\left(-\xi^2\right) d\xi = \begin{cases} 2^n n!\sqrt{\pi} & n = m \\ 0 & n \neq m \end{cases} \tag{S.6}$$

Hence the integral in Eq (S.5) vanishes unless $i = j+1$ or $i = j-1$. Thus, $\mathbf{Q_s}$ is a tridiagonal matrix. The principal diagonal is zero, and the upper and lower adjacent diagonals are non-zero. The non-zero matrix elements are then determined as follows.

For the case of $i = j+1$ we the have

$$
\begin{aligned}
\left(\mathbf{Q_s}\right)_{j+1,j} &= \frac{N_{j+1}N_j}{\alpha_s^2}\begin{Bmatrix} 2j\int_{-\infty}^{+\infty} H_{j+1}^s(\xi)\, H_{j-1}^s(\xi)\ \exp\left(-\xi^2\right)d\xi + \\ \frac{1}{2}\int_{-\infty}^{+\infty} H_{j+1}^s(\xi)\, H_{j+1}^s(\xi)\ \exp\left(-\xi^2\right)d\xi \end{Bmatrix} \\
&= \frac{N_{j+1}N_{j+1}}{2\alpha_s^2}\left[2^{j+1}\left(j+1\right)!\sqrt{\pi}\right] \\
&= \frac{1}{\alpha_s}\sqrt{\frac{j+1}{2}} \\
&= \sqrt{\frac{\hbar\left(j+1\right)}{2\omega_s}}
\end{aligned} \tag{S.7}
$$

Similarly, for the case of $i = j-1$

$$
\begin{aligned}
\left(\mathbf{Q_s}\right)_{j-1,j} &= \frac{N_{j-1}N_j}{2\alpha_s^2}\begin{Bmatrix} 2j\int_{-\infty}^{+\infty} H_{j-1}^s(\xi)\, H_{j-1}^s(\xi)\ \exp\left(-\xi^2\right)d\xi + \\ \frac{1}{2}\int_{-\infty}^{+\infty} H_{j-1}^s(\xi)\, H_{j+1}^s(\xi)\ \exp\left(-\xi^2\right)d\xi \end{Bmatrix} \\
&= \frac{N_{j-1}N_j}{2\alpha_s^2}\left(2j\right)\left[2^{j-1}\left(j-1\right)!\sqrt{\pi}\right] \\
&= \frac{1}{\alpha_s}\sqrt{\frac{j}{2}} \\
&= \sqrt{\frac{\hbar j}{2\omega_s}}
\end{aligned} \tag{S.8}
$$

Where the definition of α_s in Eq (S.1) has been used.

B. Exact Fitting Procedure for the components of the 1MR intrinsic potential

Determining the a_n coefficients can be done thru standard methods of linear algebra. To elaborate this idea, let $\left\{y_{s,i},\overline{V}_s\left(y_{s,i}\right)\right\}$ be the set of data points obtained thru direct-dynamics of the system. Using Eq (17) from the main text, a system of linear equations is formed.

$$\overline{V}_s\left(y_{s,i}\right)=\sum_{n=0}^{M-1}a_n y_{s,i}^n \ , \qquad i=1 \text{ to } M \tag{S.9}$$

or in matrix form.

$$\overline{\mathbf{V}}_\mathbf{s}=\mathbf{Y}_\mathbf{s}\mathbf{A}_\mathbf{s}$$

$$\begin{bmatrix} \overline{V}_s\left(y_{s,1}\right) \\ \overline{V}_s\left(y_{s,2}\right) \\ \vdots \\ \overline{V}_s\left(y_{s,M}\right) \end{bmatrix}=\begin{bmatrix} y_{s,1}^0 & y_{s,1} & y_{s,1}^2 & \cdots & y_{s,1}^{M-1} \\ y_{s,2}^0 & y_{s,2} & y_{s,2}^2 & \cdots & y_{s,2}^{M-1} \\ \vdots & \vdots & \vdots & \cdots & \vdots \\ y_{s,M}^0 & y_{s,M} & y_{s,M}^2 & \cdots & y_{s,M}^{M-1} \end{bmatrix}\begin{bmatrix} a_0 \\ a_1 \\ \vdots \\ a_{M-1} \end{bmatrix} \tag{S.10}$$

Provided that the matrix $\mathbf{Y}_\mathbf{s}$ is non-singular (i.e. $\det \mathbf{Y}_\mathbf{s} \neq 0$), $\mathbf{Y}_\mathbf{s}$ is an invertible matrix. Operating the matrix inverse $\mathbf{Y}_\mathbf{s}^{\mathbf{-1}}$ yields the column vector containing the fitting coefficients.

$$\mathbf{A}_\mathbf{s}=\begin{bmatrix} a_0 \\ a_1 \\ \vdots \\ a_{M-1} \end{bmatrix}=\mathbf{Y}_\mathbf{s}^{\mathbf{-1}}\overline{\mathbf{V}}_\mathbf{s} \tag{S.11}$$

Summing all the polynomials in the form of Eq (S.9) for all desired normal modes gives the 1-mode intrinsic potential $\overline{V}^{(1)}$.

C. Optimized Geometry of $(CH_3OH)_2H^+$ at MP2/aug-cc-pVDZ

The Cartesian coordinate in units of Bohr radius for the optimized geometry of MA conformer of $(CH_3OH)_2H^+$ obtained at MP2/aug-cc-pVDZ level of theory and basis.

Charge = +1	Multiplicity = 1		
	X (a_0)	Y (a_0)	Z (a_0)
H	2.61373866	-1.86752298	-2.045006273
H	-2.613738736	1.867521761	-2.045006814
H	-4.696089687	-1.948449331	-0.70140699
H	5.569979836	-0.784249238	1.17772582
H	4.696089713	1.948449154	-0.701407123
H	3.189853018	1.366605719	2.312004597
H	-3.189852968	-1.366605819	2.312004673
H	-5.569979764	0.784249148	1.177725852
H	-0.000000048	-0.000000085	-0.705627562
C	2.016142905	-1.026576965	-0.526571687
C	-2.016142984	1.026576871	-0.526571855
O	4.046099926	0.506576621	0.637012369
O	-4.046099871	-0.506576746	0.637012433

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D. Grid Reduction in MULTIMODE via Symmetry Consideration

Here we describe in detail how the implementations in MULTIMODE significantly reduces the required number of grid points in constructing a 4MR potential for $(CH_3OH)_2H^+$. We begin by describing the construction of the 1-mode intrinsic potential grids.

- 1-mode intrinsic potential grids

Mode	Mode Symmertry	No. of Gauss-Hermite Points	Symmetry Considerations
Q_1	A	16	16
Q_2	B	16	8
Q_3	B	16	8
Q_4	B	16	8
Total no. of grids		**64**	**40**

- 2-mode intrinsic potential grids

Mode	Mode Symmetry	No. of HEG Points per Mode	No. of HEG points per 2-mode pair	Symmetry Considerations	Reduced no. of HEG points per 2-mode pair
Q_1 & Q_2	A & B	10*10	100	10*10/2	50
Q_1 & Q_3	A & B	10*10	100	10*10/2	50
Q_1 & Q_4	A & B	10*10	100	10*10/2	50
Q_2 & Q_3	B & B	10*10	100	10*10/2	50
Q_2 & Q_4	B & B	10*10	100	10*10/2	50
Q_3 & Q_4	B & B	10*10	100	10*10/2	50
Total no. of grids			**600**		**300**

- 3-mode intrinsic potential grids

Mode	Mode Symmetry	No. of HEG Points per Mode	No. of HEG points per 3-mode group	Symmetry Considerations	Reduced no. of HEG points per 3-mode group	Further reduction using every other HEG grids
Q_1 & Q_2 & Q_3	A & B & B	10*10*10	1,000	(10*10*10)/2	500	(6*6*6)/2
Q_1 & Q_2 & Q_4	A & B & B	10*10*10	1,000	(10*10*10)/2	500	(6*6*6)/2
Q_1 & Q_3 & Q_4	A & B & B	10*10*10	1,000	(10*10*10)/2	500	(6*6*6)/2
Q_2 & Q_3 & Q_4	B & B & B	10*10*10	1,000	(10*10*10)/2	500	(6*6*6)/2
Total no. of grids			**4,000**		**2,000**	**432**

- 4-mode intrinsic potential grids

Mode	Mode Symmetry	No. of HEG Points per Mode	No. of HEG points per 4-mode group	Symmetry Considerations	Reduced no. of HEG points per 4-mode group	Further reduction using every other HEG grids
Q_1 & Q_2 & Q_3 & Q_4	A & B & B & B	10*10*10*10	10,000	(10*10*10*10)/2	5,000	(6*6*6*6)/2
Total no. of grids			**10,000**		**5,000**	**648**

E. Root Mean Square Error (RMSE) for the fits for 4MR-Sα-FG (α =1, 2)

The least squares fits were only performed for the components of the two-mode, three-mode, and four-mode intrinsic potentials. The RMSE in cm^{-1} are tabulated below.

Components of the 2MR intrinsic potential		
Two-mode grid	4MR-S1-FG	4MR-S1-FG
Q_2 and Q_1	5.36	5.38
Q_3 and Q_1	8.68×10^{-2}	9.06×10^{-2}
Q_3 and Q_2	5.24	5.25
Q_4 and Q_1	0.10	8.54×10^{-2}
Q_4 and Q_2	5.19	5.21
Q_4 and Q_3	0.10	8.78×10^{-2}
Components of the 3MR intrinsic potential		
Three-mode grid		
Q_3, Q_2, and Q_1	2.96	2.43
Q_4, Q_2, and Q_1	2.18	2.19
Q_4, Q_3, and Q_1	5.42×10^{-2}	0.67
Q_4, Q_3, and Q_2	1.89	2.22
Components of the 4MR intrinsic potential		
Four-mode grid		
Q_4, Q_3, Q_2, and Q_1	10.54	6.63

F. Investigating the Idea of Using a Sparser Grid

The least squares fits were only performed for the components of the two-mode, three-mode, and four-mode intrinsic potentials. The RMS fitting error in cm^{-1} for the sparser grids are tabulated below.

Components of the 3MR intrinsic potential (Sparser Grid)		
Three-mode grid	3MR-S1-SGB	3MR-S2-SGB
Q_3, Q_2, and Q_1	21.68	21.71
Q_4, Q_2, and Q_1	5.01	5.04
Q_4, Q_3, and Q_1	0.11	0.11
Q_4, Q_3, and Q_2	4.70	4.71
Components of the 4MR intrinsic potential (Sparser Grid)		
Four-mode grid	4MR-S1-SGB	4MR-S2-SGB
Q_4, Q_3, Q_2, and Q_1	13.50	13.53

The 3MR and 4MR VSCF/VCI frequencies for the sets of potentials defined in Table 3, which are used to investigate the strategy of picking every other HEG grids. These potentials were built at the CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ level of theory and basis.

Mode	**3MR-S2**		**4MR-S2**		
	FG	**SG[a]**	**FG**	**SGA[b]**	**SGB[c]**
Intermolecular O-O stretch	558.15	559.00	557.92	557.84	558.68
IHB stretch	863.88	864.05	863.97	863.83	863.79
Out-of-phase C-O stretch	992.97	995.84	992.73	992.56	995.39
Out-of-phase in-plane CH_3 rock	1097.14	1098.23	1095.86	1095.93	1096.77
Total number of grid points used	**2,340**	**772**	**7,340**	**2,988**	**1,420**

[a]Every other HEG points were used for the 3-mode intrinsic potential.

[b]Every other HEG points were used for the 4-mode intrinsic potential.

[c]Every other HEG points were used for the both 3-mode and 4-mode intrinsic potentials.

G. Convergence of the VSCF/VCI frequencies with the nMR representation

The $(CH_3OH)_2H^+$ MP2/aug-cc-pVDZ harmonic frequencies (in cm^{-1}) and MULTIMODE VSCF/VCI fundamental frequencies (in cm^{-1}) for 1 to 4MR using the PES from cases S1-SGB and S2-SGB. It is evident that convergence is achieved at 3MR.

S1-SGB		MP2/aug-cc-pVDZ					
Description		Harmonic	1-MR	2-MR	3-MR	4-MR	Expt.[3]
Q_1	Intermolecular O-O stretch	577.37	577.72	575.47	563.54	563.27	---
Q_2	IHB stretch	702.85	1060.99	848.94	896.25	895.85	868
Q_3	Out-of-phase C-O stretch	960.26	970.23	1045.68	1010.06	1010.15	985
Q_4	Out-of-phase in-plane CH_3 rock	1092.34	1101.20	1153.24	1117.20	1115.53	1107
S2-SGB		CCSD(T)/aug-cc-pVDZ//MP2/aug-cc-pVDZ					
Description		Harmonic	1-MR	2-MR	3-MR	4-MR	Expt.[3]
Q_1	Intermolecular O-O stretch	-	575.66	571.33	559.00	558.68	---
Q_2	IHB stretch	-	1021.42	815.27	864.05	863.79	868
Q_3	Out-of-phase C-O stretch	-	969.12	1037.24	995.84	995.39	985
Q_4	Out-of-phase in-plane CH_3 rock	-	1086.04	1132.21	1098.23	1096.77	1107

Note: The experimental values were taken from ref. 3 (see below). They are the highest peaks corresponding to each band in the triplet signature in the region 800-1200 cm^{-1}.

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(3) Roscioli, J. R.; McCunn, L. R.; Johnson, M. A. Quantum Structure of the Intermolecular Proton Bond. *Science* **2007**, *316* (5822), 249–254.