

# Fixed–Node, Importance–Sampling Diffusion Monte Carlo for vibrational structure with accurate and compact trial states

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## 1 Atomic masses

The masses of the isotopes are:

$$m_{\text{H}} = 1.0078250 \text{ AMU}$$

$$m_{\text{O}} = 15.994915 \text{ AMU}$$

$$m_{\text{D}} = 2.0141018 \text{ AMU}$$

## 2 Coordinates and basis set specification

The expansion of coordinates in the primitive internal coordinates set (**q**) are given together with the exponent of the harmonic oscillator basis set (**gam**). 14 basis functions were used for each coordinate in each calculation except for the VFCI analyses of the  $\text{H}_3^+$  systems, where 25 basis functions were used.

## 2.1 H<sub>2</sub>O

### 2.1.1 Primitive coordinates

q \ gam	30.000	30.000	20.000
r_OH	1.0000000000	0.0000000000	0.0000000000
r_OH	0.0000000000	1.0000000000	0.0000000000
a_HOH	0.0000000000	0.0000000000	1.0000000000

### 2.1.2 Optimized coordinates

q \ gam	30.000	30.000	20.000
r_OH	0.9900927428	-0.0098618967	-0.1400682108
r_OH	-0.0099525530	0.9900928055	-0.1400613549
a_HOH	0.1400617984	0.1400677673	0.9801855504

## 2.2 HDO

### 2.2.1 Primitive coordinates

q \ gam	40.000	30.000	20.000
r_OD	1.0000000000	0.0000000000	0.0000000000
r_OH	0.0000000000	1.0000000000	0.0000000000
a_HOH	0.0000000000	0.0000000000	1.0000000000

### 2.2.2 Optimized coordinates

q \ gam	40.000	30.000	20.000
r_OD	0.9910721717	-0.0487587011	-0.1240908521

r_OH	0.0258057192	0.9832810753	-0.1802564611
a_HOH	0.1308052574	0.1754449086	0.9757607641

## 2.3 $\text{H}_2\text{D}^+$

### 2.3.1 Primitive coordinates

q \ gam	20.000	20.000	45.000
r_DH	1.0000000000	0.0000000000	0.0000000000
r_DH	0.0000000000	1.0000000000	0.0000000000
a_HDH	0.0000000000	0.0000000000	1.0000000000

### 2.3.2 Optimized coordinates

q \ gam	20.000	20.000	45.000
r_DH	0.6399162200	-0.7071053400	0.3008475700
r_DH	0.6399132000	0.7071082200	0.3008472400
a_HDH	-0.4254624800	-0.0000007000	0.9049760700

## 2.4 $\text{D}_2\text{H}^+$

### 2.4.1 Primitive coordinates

q \ gam	20.000	20.000	45.000
r_HD	1.0000000000	0.0000000000	0.0000000000
r_HD	0.0000000000	1.0000000000	0.0000000000
a_DHD	0.0000000000	0.0000000000	1.0000000000

### 2.4.2 Optimized coordinates

q \ gam	20.000	20.000	45.000
r_HD	0.6371995572	-0.7071036502	0.3065634553
r_HD	0.6371936679	0.7071099121	0.3065612528
a_DHD	-0.4335446388	-0.0000004020	0.9011320914

## 3 Verification of the parameter space

Dependence of the energy for the  $\nu_1$  state (in  $\text{cm}^{-1}$ ) with  $\Delta\tau = 0.5 \text{ a.u.}$  on the parameters used for the orthogonalization correction,  $\lambda_k$ , and tolerance,  $\text{tol}$ , on  $|\psi(\vec{x})|$  (see Eq. 7 of the main text and the accompanying discussion). Values used in the present work are  $\lambda_k = 0.6$  and  $\text{tol} = 10^{-5}$ . Data has been collected as described in the main text. The  $\nu_1$  state of  $\text{D}_2\text{H}^+$  was chosen for the following analysis as the trial oc-VCI(1) states used for orthogonalization, i.e. ground state,  $\nu_3$ , and  $\nu_2$ , significantly deviate from the exact states, as judged by their variational energies.

$\lambda_k = 0.6 \text{ tol} = 10^{-5}$	$\lambda_k = 0.8 \text{ tol} = 10^{-5}$	$\lambda_k = 0.4 \text{ tol} = 10^{-5}$	$\lambda_k = 0.6 \text{ tol} = 10^{-6}$
$6340.1 \pm 0.4$	$6340.4 \pm 0.5$	$6340.3 \pm 0.5$	$6340.6 \pm 0.5$

Dependence of the energy for the  $\nu_1$  state (in  $\text{cm}^{-1}$ ) with  $\Delta\tau = 0.5 \text{ a.u.}$ ,  $\lambda_k = 0.6$ , and  $\text{tol} = 10^{-5}$  on the number of walkers (finite population bias). The error bars for 2500 walkers were computed from 40 independent runs.

5000 walkers	2500 walkers
$6340.1 \pm 0.4$	$6341.0 \pm 0.5$

## 4 Details of the algorithm

Here, details of implementation are provided.

Steps performed during simulation:

1. Initialize population:

- ground state: assign equilibrium configuration to walkers
- excited states: randomly displace atoms until required number of negative and positive walkers is collected

2. Propagate in imaginary time:

- modify configurations according to Eq. 3
- apply reweighing of Eq. 10 if desired
- excited states: eliminate walkers that attempted to cross nodal surface
- excited states: apply orthogonalization correction according to Eq. 7
- account for branching term according to Eq. 4
- compute average energy and the energy offset  $\mathcal{E}(\tau)$
- perform population control eliminating walkers with small absolute weights
- collect data if equilibration time has passed

Evaluation of wave function, local energy and quantum force:

- Wavefunction: the VSCF wavefunction is defined as in Eq. 1 and Eq. 2 of Ref. 1
- Hamiltonian  $\hat{H} = \hat{T} + \hat{V}$ :
  - potential energy term  $\hat{V}$ : black-box routine returning electronic energy given Cartesian coordinates of atoms
  - kinetic energy term  $\hat{T}$ : Cartesian coordinate operator (Eq. 8 of Ref. 1) but due to translational invariance of the trial state,  $\hat{T}\psi(\vec{x})$ , its implementation follows Eq. 11 of Ref. 1

- wavefunction gradient is evaluated directly and involves nothing else other than quantities needed to evaluate Eq. 11 of Ref. 1
- To evaluate  $\frac{\hat{H}\psi_T(\vec{x})}{\psi_T(\vec{x})}$  and  $\frac{\nabla_i\psi_T(\vec{x})}{\psi_T(\vec{x})}$  in a numerically stable way, whenever norm of wavefunction falls below  $10^{-40}$ , Eq. 8 and Eq. 9 from main text were enforced.

We note in passing that unlike Coulomb potentials, the potentials used in the present work are sufficiently smooth to avoid serious numerical issues. On the other hand, evaluation of internal-coordinate gradients may be problematic at extreme configurations. In the present work (low energy excitations), such configurations were unlikely to be sampled.

## References

- (1) Bulik, I. W.; Frisch, M. J.; Vaccaro, P. H. Vibrational self-consistent field theory using optimized curvilinear coordinates. *J. Chem. Phys.* **2017**, *147*, 044110.