

A quantum - classical simulation of a multi-surface multi-mode  
nuclear dynamics on  $C_6H_6^+$  incorporating degeneracy among  
electronic states

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**SUPPLEMENTARY MATERIAL**

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## I. THE TDDVR EQUATION OF MOTION

The expression of the TDDVR equation of motion<sup>1-14</sup> for an amplitude,  $d_{i_1 i_2 \dots i_p, l}$  on the  $l$  th surface is,

$$\begin{aligned}
i\hbar \dot{d}_{i_1 i_2 \dots i_p, l} &= \frac{1}{2} \left\{ \sum_k \dot{P}_{Q_k^c} \sqrt{\frac{\hbar}{ImA_k}} \bar{G}_{i_k i_k} \right\} d_{i_1 i_2 \dots i_p, l} + \left\{ \sum_k \frac{\mu(\dot{Q}_k^c)^2}{2} \right\} d_{i_1 i_2 \dots i_p, l} \\
&+ \sum_k \left\{ \frac{\hbar ImA_k}{2\mu} \sum_{i'_1 i'_2 \dots i'_p} \bar{F}_{i_k i'_k} d_{i'_1 i'_2 \dots i'_p, l} \prod_{k' \neq k}^p \delta_{i_k i'_k} \right\} \\
&+ V_{ll}(i_1 i_2 \dots i_p) d_{i_1 i_2 \dots i_p, l} + \sum_{l' \neq l} V_{ll'}(i_1 i_2 \dots i_p) d_{i_1 i_2 \dots i_p, l'}.
\end{aligned} \tag{1}$$

The explicit form of the matrices used in quantum equation of motion are presented as follows:

$$d_{i_1 i_2 \dots i_p, l} = c_{i_1 i_2 \dots i_p, l} \prod_{k=1}^p (A_{i_k, i_k})^{\frac{1}{2}}, \tag{2a}$$

$$A_{i_k, i'_k} = \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) \xi_n(x_{i'_k}), \tag{2b}$$

$$G_{i_k, i'_k} = \sum_{n=0}^{N_k-1} \xi_{n+1}^*(x_{i_k}) \sqrt{n+1} \xi_n(x_{i'_k}) + \sum_{n=1}^{N_k} \xi_{n-1}^*(x_{i_k}) \sqrt{n} \xi_n(x_{i'_k}), \tag{2c}$$

$$\begin{aligned}
F_{i_k, i'_k} &= \sum_{n=0}^{N_k} \xi_n^*(x_{i_k}) (2n-1) \xi_n(x_{i'_k}) - \sum_{n=0}^{N_k-2} \xi_{n+2}^*(x_{i_k}) \sqrt{(n+1)(n+2)} \xi_n(x_{i'_k}) \\
&- \sum_{n=2}^{N_k} \xi_{n-2}^*(x_{i_k}) \sqrt{n(n-1)} \xi_n(x_{i'_k}),
\end{aligned} \tag{2d}$$

$$\bar{G}_{i_k, i'_k} = \frac{G_{i_k, i'_k}}{\sqrt{A_{i_k, i_k} A_{i'_k, i'_k}}}, \tag{2e}$$

$$\bar{F}_{i_k, i'_k} = \frac{F_{i_k, i'_k}}{\sqrt{A_{i_k, i_k} A_{i'_k, i'_k}}}. \tag{2f}$$

The differential equation for quantum dynamics has the following important characteristics:

(a) The component matrices ( $\{\mathbf{A}_k\}$ ,  $\{\mathbf{G}_k\}$ ,  $\{\mathbf{F}_k\}$ ) of the TDDVR Hamiltonian [see (1)] are time - independent and need to be evaluated once for all; (b) Since the matrix,  $\{\mathbf{G}_k\}$ , are diagonal and associated with the ‘‘classical’’ variables  $\{\dot{P}_{Q_k^c}(t)\}$ , the non - linear dynamics of these ‘‘classical’’ quantities affects the convergence but not the final solution of the quantum equations of motion; (c) As the off - diagonal elements of  $\{\mathbf{F}_k\}$  matrices couple the grid - points and dominate the quantum dynamics, any non - linear ‘‘classical’’ propagation of their

associated parameters,  $\{ImA_k\}$ , is not desirable, and hence, a time - independent  $\{ImA_k\}$  is the obvious choice. The contribution of different modes on a time - dependent amplitude ( $\dot{d}_{i_1 i_2 \dots i_p, l}$ ) is evaluated independently, i.e.,  $\mathbf{F}_k$  matrix couple grid - points or basis functions of the  $k$  th mode only. Such multiplications along with the calculations on each surface demand an obvious parallelization of the algorithm reducing computational time remarkably and motivate us for persuading relatively large dimensional calculations.<sup>12,14</sup>

Moreover, the classical path equations for the  $k$  th mode, those appear along with the quantum equation of motion, can be written as

$$\dot{Q}_k^c(t) = \frac{P_{Q_k^c}(t)}{\mu}, \quad (3)$$

$$\dot{P}_{Q_k^c}(t) = -\left. \frac{dV(\{Q_k\})}{dQ_k} \right|_{Q_k(t)=Q_k^c(t)} + Q_k^F(t), \quad (4)$$

where  $Q_k^F(t)$  is the quantum force for the  $k$  th mode. A rigorous expression of  $Q_k^F(t)$  is derived by using Dirac-Frenkel variational principle,<sup>15</sup> i.e., by minimizing the following integral with respect to  $\dot{P}_{Q_k^c}$ ,

$$\begin{aligned} I &= \int (-i\hbar \frac{\partial \Xi^*(\{Q_k\}, t)}{\partial t} - H(\{P_{Q_k}\}, \{Q_k\}) \Xi^*(\{Q_k\}, t)) \\ &\times (i\hbar \frac{\partial \Xi(\{Q_k\}, t)}{\partial t} - H(\{P_{Q_k}\}, \{Q_k\}) \Xi(\{Q_k\}, t)) \prod_{k=1}^p dQ_k. \end{aligned} \quad (5)$$

The explicit expression of  $Q_k^F(t)$  thus obtained is

$$\begin{aligned} Q_k^F(t) &= \sum_l \sum_{i_1 i_2 \dots i_k i'_k \dots i_p} c_{i_1 i_2 \dots i_k i'_k \dots i_p}^*(t) c_{i_1 i_2 \dots i'_k \dots i_p}(t) \\ &\times \left\{ \frac{2(ImA_k)^2}{\mu} \left[ S_{i_k i'_k}^{(2)} \frac{S_{i_k i_k}^{(1)*}}{A_{i_k i_k}} - S_{i_k i'_k}^{(3)} \right] - \frac{\hbar ImA_k}{\mu} \left[ R_{i_k i'_k} \frac{S_{i_k i_k}^{(1)*}}{A_{i_k i_k}} - T_{i_k i'_k}^* \right] \right\} \\ &/ \left[ \sum_l \sum_{i_1 i_2 \dots i_k \dots i_p} c_{i_1 i_2 \dots i_k \dots i_p}^*(t) c_{i_1 i_2 \dots i_k \dots i_p}(t) \frac{S_{i_k i_k}^{(1)*} S_{i_k i_k}^{(1)}}{A_{i_k i_k}} \right. \\ &\left. - \sum_i \sum_{i_1 i_2 \dots i_k i'_k \dots i_p} c_{i_1 i_2 \dots i_k \dots i_p}^*(t) c_{i_1 i_2 \dots i'_k \dots i_p}(t) S_{i_k i'_k}^{*(2)} \right], \end{aligned} \quad (6)$$

The explicit form of  $R$ ,  $S^{(n)}$  and  $T$  matrices are

$$\begin{aligned}
R_{i_k i'_k} &= \sum_p \xi_p^*(x_{i_k}) \xi_p(x_{i'_k}) 2p, \\
S_{i_k i'_k}^{(n)} &= \sum_{pq} \xi_p^*(x_{i_k}) \xi_q(x_{i'_k}) \int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t))^n \Phi_q(Q_k, t) dQ_k, \\
T_{i_k i'_k} &= \sum_{pq} \xi_p(x_{i_k}) \xi_q^*(x_{i'_k}) 2p \int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t)) \Phi_q(Q_k, t) dQ_k,
\end{aligned} \tag{7}$$

with

$$\begin{aligned}
\int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t)) \Phi_q(Q_k, t) dQ_k &= \frac{1}{2} \sqrt{\frac{\hbar}{ImA_k}} \{ \sqrt{p+1} \delta_{p+1,q} + \sqrt{p} \delta_{p-1,q} \}, \\
\int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t))^2 \Phi_q(Q_k, t) dQ_k &= \frac{\hbar}{4ImA_k} \times \{ \sqrt{(p+1)(p+2)} \delta_{p+2,q} \\
&\quad + (2p+1) \delta_{p,q} + \sqrt{p(p-1)} \delta_{p-2,q} \}, \\
\int \Phi_p^*(Q_k, t) (Q_k - Q_k^c(t))^3 \Phi_q(Q_k, t) dQ_k &= \frac{1}{8} \left( \frac{\hbar}{ImA_k} \right)^{3/2} \times \{ \sqrt{(p+1)(p+2)(p+3)} \delta_{p+3,q} \\
&\quad + 3(p+1) \sqrt{p+1} \delta_{p+1,q} + 3p \sqrt{p} \delta_{p-1,q} \\
&\quad + \sqrt{p(p-1)(p-2)} \delta_{p-3,q} \}.
\end{aligned} \tag{8}$$

The matrices,  $R$ ,  $S^{(n)}$  and  $T$  are time - independent and need to be calculated once for all the time. It is important to note that the time - dependence of  $Q_k^F$  arises from the coefficients  $\{c_{i_1 i_2 \dots i_k \dots i_p, l}(t)\}$  only.

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