

Supplementary Materials for: A diabaticization method based upon integrating the diabatic potential gradient difference

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Supplementary Text

Fig. S1. The adiabatic energy curves in the 4-state model.

Fig. S2. Two groups of quasi-diabatic potential energy curves in the 4-state model.

Fig. S3. The mixing angles obtained by the pairwise quasi-diabatization.

Fig. S4. The newly obtained diabatic potential curves.

Supplementary Text

We use a simplified model to demonstrate the capability of our method in multi-state diabaticization. In the model, we construct four potential curves to represent the potential energies of 4 adiabatic states for a diatomic system, assume the corresponding derivative couplings with specific functions, and then perform multi-state diabaticization using the methods described in Section 2.1.

The assumed original data include adiabatic potential energies, gradient of energies and derivative couplings. The adiabatic potential energy curves (PECs), shown in Figure S1, are constructed using 4 Morse functions with different parameters. They could embody some common scenarios that occur in the multi-state systems, including:

- a typical avoided crossing, at $r = 1.42 \text{ a.u.}$
- an avoided crossing in the region of high potential energy, at $r = 0.08 \text{ a.u.}$
- multiple avoided crossings within a small area, in $r \in (1,2) \text{ a.u.}$ area
- a convergence of two states to a degenerate state, in $r > 5 \text{ a.u.}$ area
- a natural crossing between states of different symmetry, at $r = 3.57 \text{ a.u.}$

The gradient of energies and energy differences are calculated by differentiating the energies in a sufficiently small bond length. The derivative couplings are assumed according to the difference and the gradient of difference between each pair of states, and are modified to ensure that the avoided crossings can be transformed to crossings. As for E_4^g , which stands for an electronic state that has different symmetry, does not interact with the others, the derivative couplings related to it are set to 0.

We performed 2-state quasi-diabaticization between adiabatic state 1,2 and adiabatic state 2,3 using the diabaticization method based upon integrating the diabatic potential gradient difference mentioned in Section 2.1. The results of quasi-diabatic energies are shown in Figure S2. The same mathematical process is also applied between the adiabatic states 1 and 3, though the interaction between them is very weak. The new energies, along with the off-diagonal terms of the DPEM are used to calculate the pairwise mixing angles via Eq. 24, the results are shown in Figure S3. By now, the mixing angles are still not ready for the multi-state diabaticization, because the states they actually stand for will change when either of the diabatic states intersect with another. So we need to make a judgement, and in this case, the mixing angle $\lambda_{1,3}$ and $\lambda_{2,3}$ are interchanged according to the state they actually stands for after the quasi-diabaticization between adiabatic states 1 and 2. Then the ADT matrix and the DPEM are obtained via the method mentioned in Section 2.1. The diabatic PECs, as can be seen in Figure S4, are reasonable and smooth. The continuity of the diabatic PECs for both states are also shown.

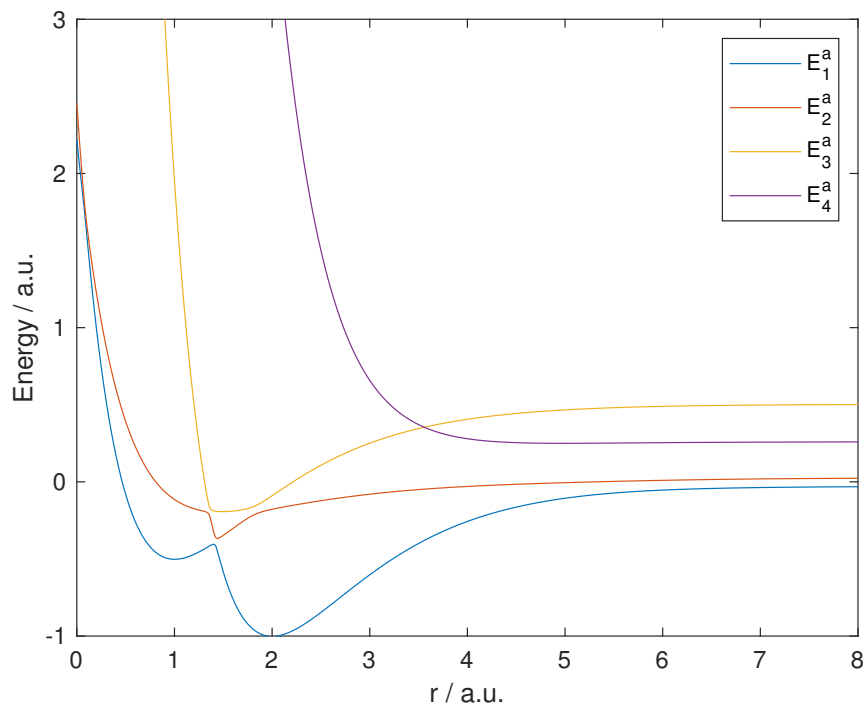


Fig. S1 The adiabatic energy curves in the 4-state model.

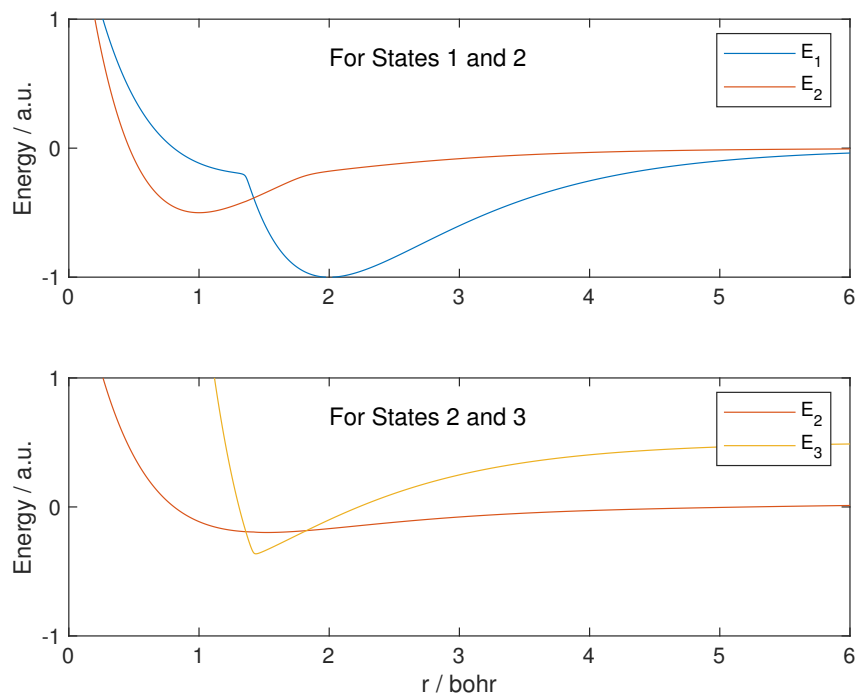


Fig. S2 Two groups of quasi-diabatic potential energy curves in the 4-state model.

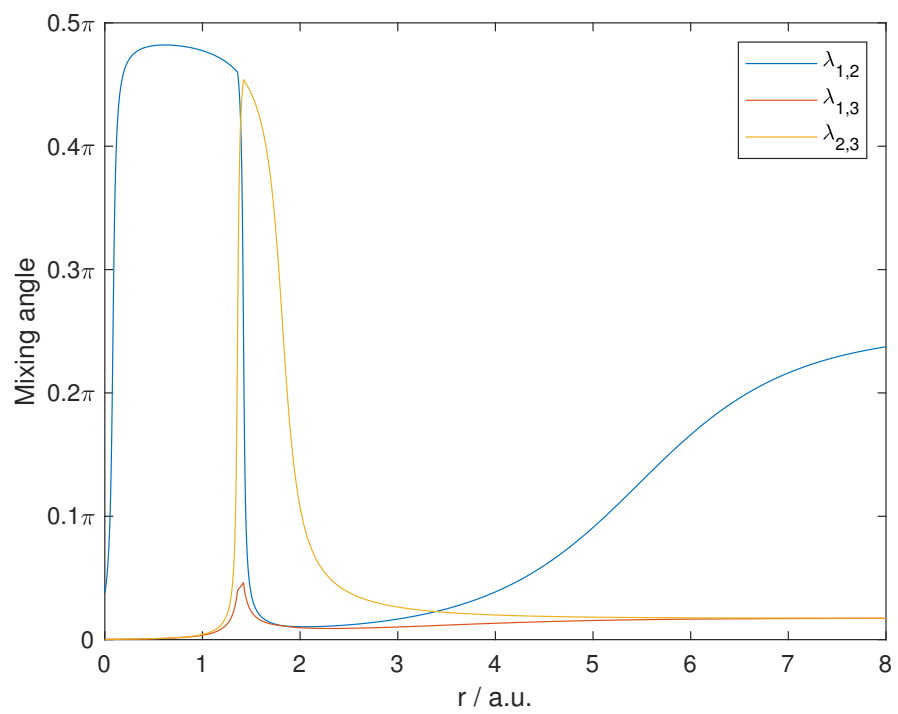


Fig. S3 The mixing angles obtained by the pairwise quasi-diabatization.

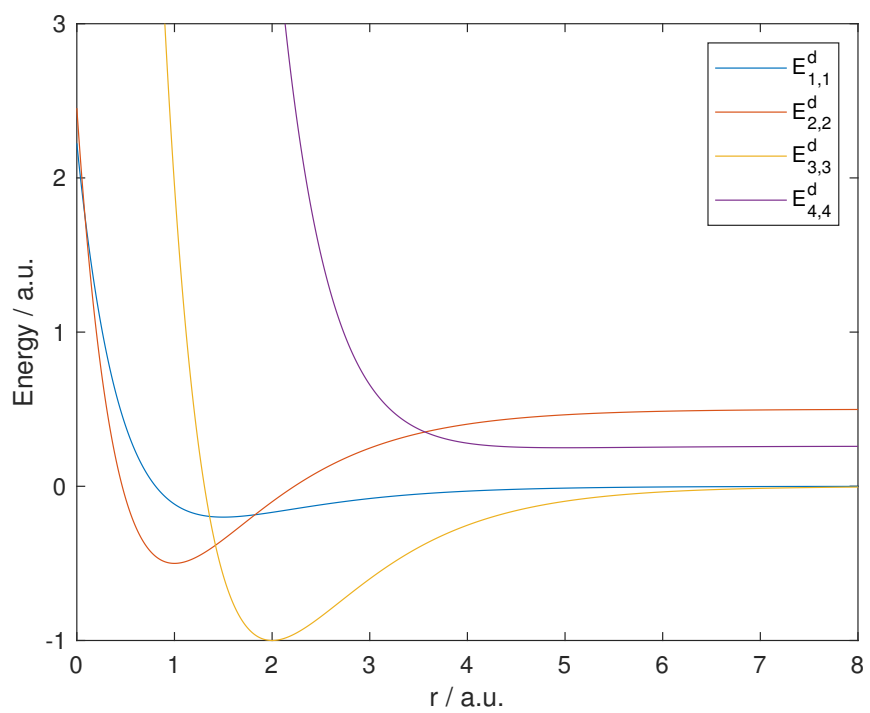


Fig. S4 The newly obtained diabatic potential curves.