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Description of the Chemical Reaction Path in the HCO Molecule: A Combined Configuration Interaction and Tight-Binding Approach

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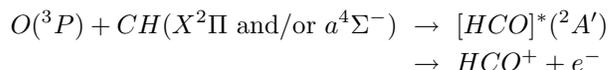
It is demonstrated that the reaction path for a polyatomic molecule (applied to the HCO molecule) is easily calculated via geometry-independent tight binding Hamiltonian fitted to accurate *ab-initio* configuration interaction (CI) total energies. This Hamiltonian not only reproduces the CI calculations accurately and efficiently, but also effectively corrects any CI energies happening to erroneously converge to excited states.

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The question. The determination of the reaction path in a chemical reaction needs the detailed knowledge of the pertinent potential energy surface (PES) (diabatic or adiabatic). This is a formidable task because (i) the PES is a multi-dimensional surface, impossible to be *ab-initio* calculated at every point in the degrees of freedom (DOF) space, and interpolation is necessary (the most accurate known detailed multi-dimensional PES is that of H₃ interpolated from 71969 *ab-initio* DOF points [1]). (ii) Because the standard *ab-initio* calculations of the many electron problem in the Born-Oppenheimer approximation, based on the variational principle, (accurate *ab-initio* configuration interaction (CI) calculations) yield only adiabatic curves, and, more importantly, being iterative, sometimes converge to undesirable states ([2], also c.f. below). Yet, such calculations may be inhibitive time consuming. For the ground state, the time problem is already traditionally overcome via the density functional theory (DFT) [3], which self-consistently approximates the many electron by a one-electron problem. However, DFT calculations sometimes fail to explain experimentally observed features of the PES [4]. Thus, the accurate CI calculations are more or less indispensable, even if performed in a rather limited, but representative, set of molecular geometries. Therefore, a reliable interpolation scheme for the pertinent PES, based on CI calculations, and overcoming the problem of wrong CI convergence, is desirable.

The purpose. It is shown that such an interpolation scheme is possible, based on a spin-polarized [5] geometry-independent [6] Slater - Koster (SK) parametrization [7] of *ab-initio* CI total energies [8]. As a demonstration, the method is applied to a triatomic molecule of chemical kinetics interest, HCO, which is an intermediate radical in the generation of a primary ion

during hydrocarbon combustion:



The reaction of O(³P) with CH(X²Π, a⁴Σ⁻) is known experimentally [9] to generate the HCO⁺ cation via autoionization of some state (or states) of the intermediate HCO radical upon interaction with some vibrational level of the ion. The first step toward computations of such interactions is the construction of the potential energy surface (PES) of the states with low (or no) barrier, through which a reaction at the experimental temperature can proceed. Such a state (without a barrier) is the HCO(X²A') state [10], used here to test the interpolation scheme on a molecular system. The reaction path of the formation of HCO (in ²A' symmetry) is also computed using the interpolated PES.

The procedure. First several (724 - compared to 71969 of H₃ [1]) accurate CI total energies, based on (less accurate) multi-configuration self-consistent field (MC-SCF) orbitals, are calculated at selected geometries of the H,C,O atoms in the A' symmetry of the Cs group. Most of them (508) are fitted to the interpolation scheme, the remaining serving to check the quality of the fit. For the fit a non-orthogonal spin-polarized tight binding (TB) Hamiltonian is formed, whose matrix elements, along with those of the overlap matrix, are expressed as functions of the bond direction, according to the SK scheme [7], and of the bond length, according to the Naval Research Laboratory (NRL) technique [6], i.e.: The functions are generally polynomials of the interatomic distance, within exponential envelopes, the coefficients and the exponents being varied as parameters. For two adiabatic states near some (avoided) crossing the TB Hamiltonian naturally produces two diabatic PESs in nearby extrapolation, and predicts to which diabatic PES, ground-state or excited, nearby CI energies belong. Among these, the appropriate ones can be used to ex-

tend the fit beyond the (avoided) crossings, around which two sets of parameters are needed for the two PES's. If it happens, as with HCO, that the ground and excited state energies beyond the crossing lie close to each other, the adiabatic PES can be fitted as well, with comparable accuracy.

Finally, by using at each point of the DOF space the lowest lying TB-fitted PES, the adiabatic path can be found: For each value of a desired degree of freedom (in our case for each C-O distance) the energy minimum is searched [11] in the space of the remaining degrees of freedom (C-H distance and H-C-O angle). Having the parametrized tight binding Hamiltonian, any property can be trivially computed.

Methodology. For the CI energies the correlation consistent aug-cc-pVTZ basis set was used [12, 13] in conjunction with the complete active space self-consistent field (CASSCF) + 1 + 2 multi-reference CI method (MRCI) employed in the MOLPRO package [8] (the four electrons in the 1s orbitals of C and O were unexcited). The CASSCF calculations were state-averaged, and the active space was limited to the 9 valence orbitals among which the remaining 11 electrons were distributed. In the subsequent MRCI calculations the uncontracted configurations were around 50 million internally contracted to about one million. Calculations between C-O distances of 1.7 and 6 bohr were done for several H-C-O angles between 50° and 180° and several C-H distances between 1.7 and 4.5 bohr, most around the C-H equilibrium distance of 2.12 bohr. The three lowest roots of the secular equation were computed to increase the accuracy of the calculation. By an analytic gradient optimization at the MCSCF level, an approximate (MCSCF) equilibrium geometry was found at the DOF space point $(\tilde{r}_{HC}, \tilde{r}_{CO}, \tilde{\theta}_{H-C-O}) = (2.12, 2.2, 126^\circ)$ (in a.u.). Because it is not evident whether the aforementioned points are beyond any avoided crossing, where the role of the ground and the excited states would be interchanged, first several DOF points near equilibrium were obtained by employing a generalization of the 3-dimensional sphere to the generally multi-dimensional (in this case also 3-dimensional) DOF space: $x_i = r_i/\tilde{r}_i - 1$, $i = \{\text{HC, CO}\}$, $x_3 = \theta/\tilde{\theta} - 1$, where generally for n degrees of freedom, points belonging to a n -dimensional hypersphere of radius r and center $(\tilde{x}_i, i = 1, \dots, n)$ are obtained by

$$\begin{aligned} x_n - \tilde{x}_n &= r \cos\theta_n \\ x_{n-1} - \tilde{x}_{n-1} &= r \sin\theta_n \cos\theta_{n-1} \\ &\dots \\ x_1 - \tilde{x}_1 &= r \sin\theta_n \sin\theta_{n-1} \dots \cos\theta_1 \end{aligned} \quad (1)$$

where the 1st $\theta_1 = 0$ or 180° , the two points of a "1-dimensional sphere", and the other $0 < \theta_i < 180^\circ$ are the "azimuthal" hypersphere angles (incidentally, a *variable dimensional* do-loop code was invented, needed to treat any larger molecule). Thus, first points with small r were fitted, and gradually the fit was extended to more remote

DOF points.

The formalism of the NRL geometry - independent TB parametrization is described in detail in Ref. [6]; here an essential summary is only presented. The total energy is written as

$$\begin{aligned} E[n(\vec{r})] &= \sum_{i; s=1,2} f\left(\frac{\mu - \epsilon_{i s}}{T}\right) \epsilon_{i s} + F[n(\vec{r})] \\ &\equiv \sum_{i; s=1,2} f\left(\frac{\mu' - \epsilon'_{i s}}{T}\right) \epsilon'_{i s} \end{aligned} \quad (2)$$

where [14] $f(x) = 1/(1 + e^x)$, $T=0.005$ mRy, and

$$\epsilon'_{i s} = \epsilon_{i s} + V_0 \quad ; \quad \mu' = \mu + V_0 \quad ; \quad V_0 = F[n(\vec{r})]/N_e \quad (3)$$

with $N_e = \sum_{i; s=1,2} f((\mu - \epsilon_{i s})/T)$ being the number of electrons, i counts the states, $s = 1, 2$ counts the spin. Since the total energy is independent of the choice of zero of the potential, the shift V_0 is sufficient to be determined by the requirement that $\epsilon'_{i s}$ are the eigenvalues of the generalized eigenvalue problem $(\mathbf{H} - \mathbf{S} \epsilon'_{i s}) \psi_{i s} = 0$, where \mathbf{H} is the TB Hamiltonian and \mathbf{S} is overlap matrix in an atomic s- and p-orbital basis representation $\{\phi_a\}$. Thus, a non-orthogonal TB calculation uses on-site, hopping and overlap parameters. Demanding that only the on-site SK parameters are affected by the shift V_0 , for atom I in a spin-polarized structure the matrix elements are expressed as

$$h_{l s}^I = \sum_{n=0}^3 b_{l n s}^I \varrho_{I s}^{2n/3} \quad ; \quad l = s, p \quad (4)$$

where

$$\varrho_{I s} = \sum_{J \neq I} e^{-\lambda_{\bar{I} \bar{J} s} R_{I J}} f\left(\frac{R_{I J} - R_0}{r_c}\right) \quad (5)$$

is a generalized pair potential ("density"), with $R_0 = 15$ bohr, $r_c = 0.5$ bohr, $R_{I J}$ is the internuclear distance between atoms I and J , $\bar{I}(\bar{J})$ denote the type of atom on the site $I(J)$ while $\lambda_{\bar{I} \bar{J} s}$, depending on the atom type, and $b_{l n s}^I$ are the on-site NRL geometry-independent parameters (GIP). It is found sufficient to keep hopping and overlap parameters spin independent, of the form

$$P_\gamma(R) = \left(\sum_{n=0}^2 c_{\gamma n} R^n \right) e^{-g_\gamma^2 R} f\left(\frac{R - R_0}{r_c}\right) \quad (6)$$

where γ indicates the type of interaction (i.e. $ss\sigma$, $sp\sigma$, $pp\sigma$, $pp\pi$ and $ps\sigma$). The NRL GIPs are $c_{\gamma n}$ and g_γ , R is the interatomic distance, and R_0 and r_c are as in eq. 5.

Within the context of the NRL code [6], written primarily for solids, the molecule was treated as a base to a large cubic lattice unit cell (lattice constant = 100 a.u.) ensuring vanishing interaction between atoms in neighboring cells. Thus, the PES was described in terms of

the following NRL GIPs for each spin polarization. On-site: s: H, C, O, (H depending on C), (C on H), (H on O), (O on H), (C on O), and (O on C); p: C, O, (C on H), (O on H), (C on O), and (O on C). Hopping and overlap parameters: $ss\sigma$: H-C, H-O, C-O; $sp\sigma$: H-C, H-O, C-O and O-C (denoted as $ps\sigma$); $pp\sigma$ and $pp\pi$: C-O. For HCO, since similar atoms are well separated, the H-H, C-C and O-O parameters vanish. We fitted 508 CI points and checked the resulting PES against 216 more CI energies not included in the fit. The error was less than 10^{-3} a.u., which is within the *ab-initio* PES accuracy (starting from different initial guesses the MCSCF calculation may converge to slightly different results by 10^{-3} a.u.). To ensure obtaining physically meaningful TB parameters, for a very limited number of molecular geometries the Hamiltonian eigenvalues were also fitted, while the total energy was fitted for all 508 structures.

Finally, for the reaction path we used a non-linear energy minimization technique employing Powell's conjugate directions method [15] modified to be restricted to closed intervals of the DOF space [11].

For comparison, each of the 724 *ab-initio* CI calculations needs 3 hours of CPU time, each n -dimensional hypersphere radius r -increase, to fit more remote points (with 10 such hypersphere radial extensions all points can be covered) needs 2-3 hours, and each 2-dimensional energy minimization, using the final TB parameters (i.e. the reaction path determination), needs a few seconds.

Results. The fitted TB Hamiltonian could predict cor-

rectly total energy curves for points not included in the fit as shown for example in Fig. 1. Since it produces naturally the diabatically extended branch of the energy, it could distinguish to which adiabatic state near an avoided crossing the CI values belong. Classifying such CI points may sometimes be misleading or unrecognizable by mere observation of the MCSCF orbitals. An example is shown in Fig. 2. However, the most impressive aspect was that we realized, through the fit, that at some points (about 10 in 700) the CI calculation had converged to *excited* energies (which ought to be disregarded, otherwise they would destroy the fit). An example is given in Fig. 3. Finally, Fig. 4 shows the reaction path for the formation of HCO, as HC approaches O. For a triatomic molecule the figure contains the whole information: For each C-O distance the minimum energy and the corresponding C-H distance and H-C-O angle are displayed. At large C-O distances, O is more attracted toward H, but, in approaching equilibrium, O binds mainly with C, the H-C-O angle gradually becoming $\simeq 122^\circ$ (representing the CI value). Around equilibrium (c.f. Table I), the angle changes slightly monotonically by $1-2^\circ$, but because, in increasing the C-O distance, the C-H distance decreases, predominantly an antisymmetric stretching vibration occurs. To our knowledge there is no experimental confirmation of the reaction path of this intermediate molecule.

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TABLE I: Geometric characteristics of HCO around equilibrium, along the reaction path, in a.u. (H-C-O angle in degrees). The last three columns indicate the minimum energy molecular geometry.

C-O distance	Total Energy	C-H distance	H-C-O angle
2.6	-113.6328	2.069	117.53
2.5	-113.6485	2.071	118.69
2.4	-113.6610	2.077	119.77
2.3	-113.6685	2.088	120.84
2.2	-113.6687	2.107	121.91
2.1	-113.6583	2.130	122.98
2.0	-113.6326	2.153	124.09

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Fig.1a

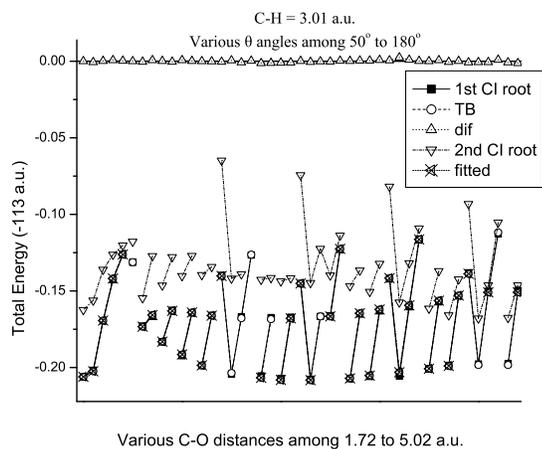


Fig.1b

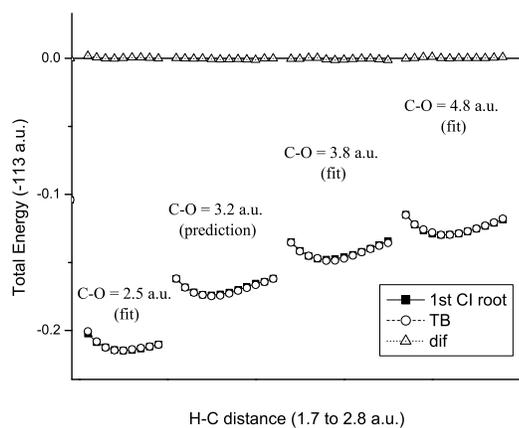


FIG. 1: Predicted total energy E in a.u. (Above:) vs C-O distance for C-H distance = 3.01 bohr, and various H-C-O angles. (Below:) vs C-H distance for various C-O distances, and H-C-O angle = 100° .

Fig.2

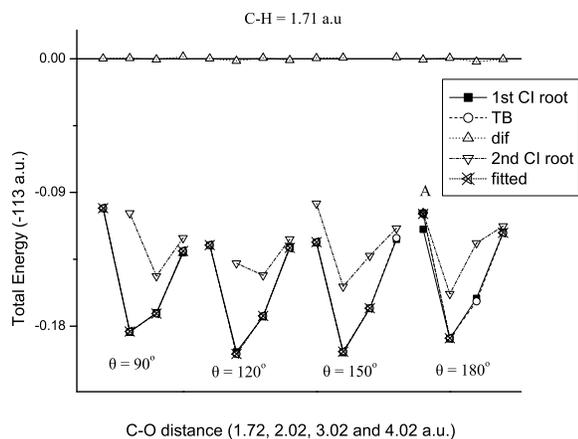


FIG. 2: The CI point A (excited) in E vs C-O distance for C-H distance = 1.71 bohr and H-C-O angle = 180° is predicted by the fit to belong to the diabatic branch of the curve beyond the avoided crossing. (Inclusion of the lower value to the fit, destroys it.)

Fig.3

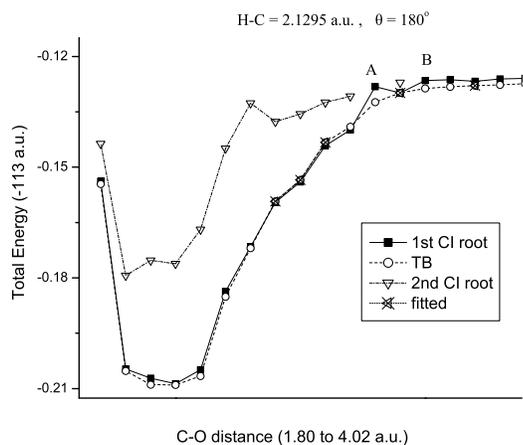


FIG. 3: The CI points A and B clearly belong to the excited state as shown by the TB prediction. The CI calculation could not converge to the correct values. The discontinuity can be verified by observing the corresponding MCSCF orbitals.

Fig.4

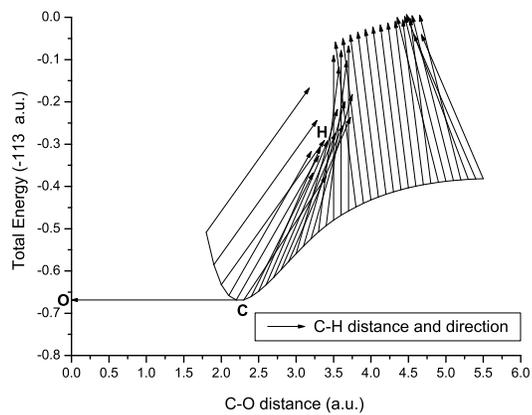


FIG. 4: The reaction path for the formation of HCO. Details are described in the text.