

Potential energy functions for high-energy collisions of atmospheric gases and their dissociation products

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Dissociation, reaction, and energy transfer in high-energy collisions of N₂, O₂, N, and O are important for hypersonic flight simulations. We have been developing potential energy surfaces for such collisions in two stages: (1) uncoupled potential energy surfaces for electronically adiabatic collisions of molecules and atoms in their ground electronic states; (2) coupled potential energy surfaces for electronically excited collision partners and electronically inelastic collisions. Stage 2 is in progress; this talk will focus on stage 1, which is almost complete.

Potential energies are generated by

- Dynamically weighted state-averaged complete active space self-consistent Field (DW-SA-CASSCF) including all 2p electrons in the active spaces
- Complete active space second-order perturbation theory (CASPT2)
- Dynamical scaled external correlation (DSEC)

Surfaces are fit by

- in all cases:
 Many-body permutationally invariant polynomials in mixed-exponential-Gaussian bond order variables (MB-PIP-MEG)
- in some cases, also by:
 - • Permutationally invariant polynomial neural network (PIP-NN)
 - • Statistically localized, permutationally invariant, local interpolating moving least squares (L-IMLS-G2)

Because of the open-shell character of N, O, and O₂, the collisions of ground-state species takes place on multiple potential energy surfaces (except for N₂ + N₂ collisions, which occur on single surface). For example, O (³P) + O₂ (X ³Σ_g⁻) collisions occur on nine potential energy surfaces with the following weights:

$$\begin{aligned} & \frac{1}{27} [O_3(1^1A') + O_3(2^1A') + O_3(1^1A'')] \\ & + \frac{1}{9} [O_3(1^3A') + O_3(2^3A') + O_3(1^3A'')] \\ & + \frac{5}{27} [O_3(1^5A') + O_3(2^5A') + O_3(1^5A'')] \end{aligned}$$

The following cases are done: N₂ + N₂, N₂ + O₂, O₂ + O₂, O + N₂, O + O₂, and N + O₂.

The case of $N + N_2$ is almost finished.