

# *Ab initio* Curly Arrows and Reaction Orbitals

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Curly arrows are most commonly used without any quantitative justification. A necessary assumption for their use, were one to present any at all, might be that most molecular orbitals in a system need not be considered, as their contribution to the overall energy remains constant during a chemical reaction. Using simple Fock eigenvalues, it is easy to show that this is not true. In most cases, even core orbitals experience significant energy changes with reaction coordinate, because of electrostatic effects. To bridge the gap between *ab initio* wavefunctions and curly arrows, we propose to partition the energy into a global potential energy and a remaining energy arising from covalency, then further partition the latter into orbital contributions - the majority of which are not expected to experience strong energy changes - and consequently remove any concern attached to the aforementioned assumption. Should further concentration of the covalent energy changes be necessary, minimisation of a functional exploiting the rotational invariance of the Hartree-Fock energy is considered. Potential energy associated with the variational relaxation of the molecular orbitals as basis set size is increased is kept as part of the covalent energy by projecting onto a minimal basis set and back again, as is done in some orbital localisation routines (Knizia, JCTC 9 (2013) 4834), and taking the energy of these orbitals interacting with each other, and with the nuclei, as being the global potential. The orbitals whose covalent energy changes strongly are the “reaction orbitals”, with whom curly arrows are drawn in tandem.