σ-π Separation of Diatomic Interaction Energies

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For Mayer bond orders B^{AB} [1], separation of components belonging to different irreducible representations can be done rigorously when the atoms *A* and *B* lie on a symmetry plane or axis [2]. We demonstrate that the symmetrized bond orders B_σ^{AB} and B_π^{AB} can be expressed through symmetrized "Mulliken" one-atom densities $\rho_\sigma^A(\mathbf{r}|\mathbf{r}')$ and $\rho_\pi^A(\mathbf{r}|\mathbf{r}')$ as follows:

$$\rho_\sigma^A(\mathbf{r} \mid \mathbf{r}') = \sum_{\mu\in A}^{\sigma} \sum_{\nu}^{\text{all}} D_{\mu\nu}\chi_\nu(\mathbf{r})\chi_\mu(\mathbf{r}')$$

$$B_\sigma^{AB} = \frac{1}{2}\iint \rho_\sigma^A(\mathbf{r} \mid \mathbf{r}')\rho_\sigma^B(\mathbf{r}' \mid \mathbf{r})\, d\mathbf{r}\, d\mathbf{r}'$$

A similar symmetry partition for Mayer diatomic energies [3, 4] is not straightforward, but in principle can be also done by inserting $\rho_\sigma^A(\mathbf{r}|\mathbf{r}')$ and $\rho_\pi^A(\mathbf{r}|\mathbf{r}')$ into the Hartree–Fock energy expression. Both pure σ- and π- and σ-π-cross-terms emerge. The main question in such a separation is how to partition the nuclear repulsion $1/R_AR_B$.

The approach is illustrated by several numerical examples.

References

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