

Hückel Model Hamiltonian

The Hückel Hamiltonian

The Hamiltonian is a one-electron site-interaction model, with one orbital (traditionally a π orbital) per site.

$$\hat{H} = \sum_{p,q=1}^n h_{pq} a_p^\dagger a_q$$

- (1) Traditionally there are two parameters: - an α_{pp} parameter that is the diagonal terms, representing the energy associated with an electron on the site p - a $\beta_{pq} = \beta_{qp}$ parameter that is the resonance/hopping/bond term between sites p and q .

Note: Traditionally Hückel theory works by assuming that orbitals on different sites do not overlap. Hückel Hamiltonians are always restricted but we do support the imposition of an external magnetic field.

Traditionally, the values of α and β are defined for the 2p orbital in an sp^2 hybridized carbon atom, with reasonable values being:

$$\alpha = -11.26 \text{ eV} = -0.414 \text{ Hartree}$$

(2)

$$\beta = -1.45 \text{ eV} = -0.0533 \text{ Hartree}$$

- (3) The α value is chosen from the binding energy (minus one times the ionization potential) of the Carbon atom; the β value is defined by Rauk based on the carbon-carbon bond strength in ethylene, and is on the high end of the “accepted” range of values. For heteroatoms, these values are shifted by:

$$\alpha_X = \alpha + h_X \cdot |\beta|$$

(4)

$$\beta_{XY} = k_{XY} |\beta|$$

- (5) A table of these values is given by Rauk.

An alternative approach in which the Wolfsberg-Helmholz approximation is used to define β_{XY} is also supported.

$$\beta_{XY} = 1.75 S_{XY} \frac{\alpha_X + \alpha_Y}{2}$$

To use the Wolfsberg-Helmholz approximation, the overlap between the orbitals, S_{XY} must be specified. However, S_{XY} can be deduced from the distance between the sites and/or from atom-types and mean bond distances.

Input Formats

API

- Connectivity can be provided in the usual way, as a lattice, an adjacency matrix, a distance matrix, or explicit connectivity specification.
- Parameters can be specified as a matrix or a dictionaries (for α_X and/or β_{XY}). The default dictionaries invoke either Rauk's parameters (for his atom-types) or the usual default parameters (based on atomic ionization potentials and electron affinities).
- Proposed Calling Sequence:

```
modelh.Huckel(connectivity, alpha=, beta=, atom_types=None, atom_dictionary=None, bond_
```

```
"""Compute the 1-electron integrals associated with the Hueckle Hamiltonian.
```

```
h_{pq} = alpha_p      p = q
        = beta_{pq}   p \ne q
```

Parameters

connectivity

an object specifying molecular connectivity

alpha

If alpha is a float, it specifies the site energy if all sites are equivalent.
Default value is the 2p-pi orbital of Carbon.

beta

If beta is a float, it specifies the resonance energy if all bonds are equivalent.
The default value is appropriate for a pi-bond between Carbon atoms.

atom_types

A list of dimension equal to the number of sites specifying the atom type of each s
If a list of atom types is specified, the values of alpha and beta are ignored.

atom_dictionary

Contains information about alpha values for each atom type.

bond_dictionary

Contains information about beta values for each bond type.

Bz

External magnetic field in atomic units.

Returns

integrals_1el

One-electron integrals.

Restricted or Unrestricted or Generalized?

Hückel theory always uses restricted Hamiltonians. So $h_{p\alpha q\alpha} = h_{p\beta q\beta}$ and $h_{p\alpha q\beta} = h_{p\beta q\alpha} = 0$.

References

- Parameters from [Arvi Rauk, The Orbital Interaction Theory of Organic Chemistry](#) , Second Edition, Wiley-Interscience, New York, 2001..
- Overlaps of orbitals from [R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, "Formulas and Numerical Tables for Overlap Integrals", *J. Chem. Phys.* **17**, 1248-1267 \(1949\).](#)