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4.3.2 The Secular Equation

Variational Principle ⇒ as we get closer and closer to the "true" one-electron ground-state wave function, we will obtain lower E_0 from our guess.

- select basis set, and define coefficients a_i, which will minimize the E for all possible linear combinations of our basis functions.

To find the optimal one-electron wave functions for a molecular system:

1) Select a set of N basis functions.
2) For that of basis functions, determine all N^2 values of both H_{ij} and S_{ij}
3) Form the secular determinant, and determine the N roots E_j of the secular equation (this step permits the equation to be true)
4) For each of the N values of E_j, solve the set of linear equations to determine the basis set coefficients a_{ij} for that MO.

# of unknown $\in N$

$$\sum_{i=1}^{N} a_i (H_{ki} - E S_{ki}) = 0 \quad \forall k$$

a_i: coefficient; H_{ki}: resonance integral; E: energy; S_{ki}: overlap integral