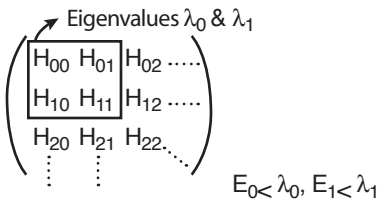
The Hylleraas-Undheim theorem (all states) and variational principle (ground state):

ex: picking a 2x2 matrix out of a large matrix sorted so $H_{00}<H_{11}<H_{22}\cdots$



If you make the smaller matrix just 1x1, you get the variational principle for the ground state.

Variational principle:

$<E> = <\varphi_0 | \hat{H} | \varphi_0> \geq E_0$ for any function φ_0.

ex: (in atomic units $m_e = 1$, $\hbar = 1$, and $e^2/(4\pi\varepsilon_0 = 1)$

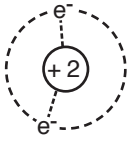
H atom	He atom
$\hat{H}_H = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} = \hat{h}_1(Z=1)$	$\hat{H}_{He} = \hat{h}_1(Z=2) + \hat{h}_2(Z=2) + \frac{1}{r_{12}}$
$\Psi_0 = c \cdot e^{-Zr_1}\alpha_1$	$\Psi_0 \approx \varphi_0 = c^2 \cdot e^{-Zr_1} \cdot e^{-Zr_2}(\alpha_1\beta_2 - \alpha_2\beta_1)$
$E_0 = -\frac{1}{2} a.u. = 2.17 \cdot 10^{-18}$ J	$E_0 = ?$
$E_{expt} = 2.17 \cdot 10^{-18}$ J	$E_{expt} = -2.9$ a.u. $= 1.26 \cdot 10^{-17}$ J

The He atom: defining the concept of "effective nuclear charge" using the variational principle:

Variational calculation: $Z_{eff} \approx 1.6875$

Freshman chemistry rule: $Z_{eff} = Z - \#$ inner e^- $- 1/2$ (# valence e^- $- 1$)

$= 1.5$ for He



motion correlated, lowers energy, increases Z_{eff}