Extra Notes — Vib. Spec.

Full molecular Sch. Eq.

$$\mathcal{H}\Psi(r,R) = \left[\frac{-\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha^2 - \sum_\alpha\sum_i \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{ij}\frac{e^2}{r_{ij}} + \sum_{\alpha\beta}\frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}}\right]\Psi$$

This does not separate but we can approximate

1st – solve all terms dependent on $e^-$ position: $r_i$

$$\mathcal{H}_e \phi_e(r,R) = \left[\frac{-\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{i\alpha}\frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{ij}\frac{e^2}{r_{ij}}\right]\phi_e(r,R) = U_e(R)\phi_e$$

how – ? – assume (like last chapter) that nucleii fixed

if not move then this is just same as solve for MO

approximate separability of electron (move in avg. pot.)

Solutions:

$\phi_e(r,R)$ – wavefct dep on elect coord, parametric on R, since electron attracted to nucleii

$U_e(R)$ – energy a const for const R, but move nucleii – change energy

$\Rightarrow$ method of optimize geom.

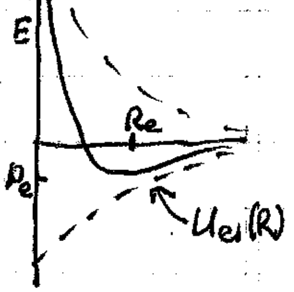
How to solve whole problem

Born Oppenheimer: $\mathcal{H}\,\Psi(rR) \approx (\mathcal{H}_e + \mathcal{H}_v)\,\phi_e(rR)\,\chi_v(R)$

$= (U_e(R) + E_v)\,\phi_e(rR)\,\chi_v$

idea is assume nuclear + electron motion separate

reasonable since masses so diff, $e^-$ relax fast to any change in nuclear position




$$\mathcal{H}_v \chi_v(R) = \Big(\overbrace{-\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2}^{T_N} + \overbrace{\sum_{\alpha\beta}\frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}}}^{V_{NN}} + U_e(R)\Big) = E_v\,\chi_v(R)$$

here $U_e(R) \rightarrow$ electron eigenvalue, is nuclear potential but due to nuclear repulsion, these are mixed / not separ