Correction of Born-oppenheimer approximation with nuclear motion

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Born-oppenheimer approximation

- The motion of atomic nuclei and electrons in a molecule can be separated.

$$\psi_{total} = \psi_{electronic} \times \psi_{nuclear}$$

- Electronic stationary Schrodinger equation:

$$H_e(r,R)\phi(r,R) = E_e\phi(r,R)$$

- Nuclear stationary Schrodinger equation:

$$\left(T + E_e(R)\right)\varphi(R) = E\varphi(R)$$

Interaction representation

- For a time dependent wave function

$$|\Psi_s(t)> = U_s(t, t_0)\ |\Psi_s(t_0)>$$

$U_s(t, t_0)$ is a transformation operator.

From Schrödinger eqn,

$$i\hbar \frac{d}{dt}|\Psi_s(t)> = H_s|\Psi_s(t)>$$

We get, $i\hbar \frac{dU_s}{dt} = H_s U_s$, so $U_s(t, t_0) = \exp(-iH_s(t - t_0)/\hbar)$

$$H_I = U_S H_S U_S^{-1}$$

Consider a nuclear motion

- In interaction representation, transformation operator:

$$U = \exp\left(\frac{iH_s t\kappa}{\hbar}\right), \kappa \textit{ is correction factor}$$

$$H_s = T_{electron} + V(x, Q_0 + Q) = H_s^0 + H_s^1(x, Q_0)Q + \frac{1}{2}H_s^2(x, Q_0)Q^2$$

Q is the nuclear displacement around Q_0

Electronic: $$H_s \phi_l(x, Q_0) = \epsilon_l(Q)\ \phi_l(x, Q_0)$$

Nuclear: $$\left(T_s + \epsilon_l(Q)\right)\varphi_{lm}(Q) = \xi_{lm}\varphi_{lm}(Q)$$

$$T_s = \frac{P^2}{2M}$$

Interaction energy

- Electronic energy, since $H_I = U_S H_S U_S^{-1}$=H_S

$$\langle \phi_l | H_I | \phi_l \rangle = \epsilon_l(Q) = \epsilon_l(Q_0) + \alpha Q + kQ^2$$

- Nuclear K.E energy,

$$\langle \phi_l | T_I | \phi_l \rangle = \langle \phi_l \big| U_S T_S U_S^{-1} | \phi_l \rangle$$

$$\cong \left\langle \phi_l \middle| \left(1 + \frac{iHst\kappa}{\hbar}\right) T_S (1 - \frac{iHst\kappa}{\hbar}) \middle| \phi_l \right\rangle$$

$$= \frac{P^2}{2M} + \frac{it\kappa}{\hbar} \langle \phi_l | [H_s, T_S] | \phi_l \rangle + \frac{(it\kappa)^2}{2\hbar^2} \langle \phi_l | [H_s, [H_S, T_S] \quad | \phi_l \rangle$$

$$= \frac{P^2}{2M} - \frac{t\kappa}{2M} \left(2\alpha P + k(QP + PQ)\right) + \frac{(t\kappa)^2}{2M} (\alpha + kQ)^2$$

Dimensionless

- $q' = Q(\frac{M\omega}{\hbar})^{1/2}, p' = P(M\omega\hbar)^{-1/2}, \dot{q}' = \omega p'$, b= $\alpha(M\omega^3\hbar)^{-1/2}, \omega^2 = \frac{k}{M'}$,

 interaction energy $\hbar\omega\boldsymbol{\eta}' = \xi_{lm}$-$\epsilon_l(Q_0)$=$\epsilon_l(Q)$+$\langle\phi_l|T_I|\phi_l\rangle$-$\epsilon_l(Q_0)$

- $\boldsymbol{\eta}'$=$\frac{1}{2}(p'^2 + q'^2) + bq' - t\kappa\omega\left(bp' + \frac{1}{2}(p'q' + q'p')\right) + \frac{1}{2}\left(t\kappa\omega(q' + b)\right)^2$

$\eta = \frac{1}{2}(p^2 + q^2) - \frac{1}{2}t\kappa\omega(pq + qp)$+$\frac{1}{2}(t\kappa\omega q)^2$, take q $= q' + b, p = p'$,

$$\boldsymbol{\eta} = \boldsymbol{\eta}' + \frac{1}{2}b^2$$

This can be taken as transformation,

$$\boldsymbol{\eta} = U_1\frac{1}{2}(p^2 + q^2)U_1^{-1},$$

$U_1 = \exp\left(i\frac{1}{2}q^2 t\kappa\omega\right) = \exp(i(\frac{1}{2}(p^2 + q^2) - q^2)t\kappa\omega)$=$\exp\left(i\frac{1}{2}p^2 t\kappa\omega\right)$.

So $\boldsymbol{\eta} = \frac{1}{2}(p^2 + (q + t\kappa\omega p)^2) = \frac{1}{2}(p^2 + (q + t\kappa\dot{q})^2) = \frac{1}{2}(p^2 + \tilde{q}^2)$

Correction factor κ

- $v_e \cong \frac{\hbar}{m_e d},\ and\ T\ is\ the\ same\ order\ with\ V, \frac{\hbar^2}{md^2} \cong \frac{e^2}{d}$
- Plus Harmonic oscillator $\mathrm{V} = M\omega^2 d^2$
- So $\omega = \frac{\hbar}{md^2}(\frac{m_e}{M})^{1/2}$
- Besides, $\Delta E \cong \frac{\hbar}{\Delta t}, \Delta t = \frac{d}{v_e} = \frac{md^2}{\hbar}$
- $\kappa = \frac{\omega}{v_e} = \frac{\hbar\omega}{\Delta E d}$