3.2.1 Conservation of Invariants

Theorem: Let the self-adjoint operator A commute with the Hamiltonian H, i.e.

$$[A, H] = AH - HA = 0.$$

If $Au \in T_u \mathcal{M} \quad \forall u \in \mathcal{M} \cap D(A)$,

then $\langle u(t) | A | u(t) \rangle = \text{const.}$

Proof: $\frac{d}{dt} \langle u | A | u \rangle = \langle \dot{u} | A | u \rangle + \langle u | A | \dot{u} \rangle =$

$$= \langle \dot{u} | A | u \rangle + \overline{\langle \dot{u} | A | u \rangle} = 2 \mathrm{Re} \langle \dot{u} | Au \rangle =$$

$$= 2 \mathrm{Re} \langle -iHu | Au \rangle = 2 \mathrm{Re} \langle u | iHAu \rangle =$$

$$= \langle u | iHAu \rangle + \overline{\langle u | iHAu \rangle} =$$

$$= \langle u | iHAu \rangle + \langle iHAu | u \rangle =$$

$$= \langle u | iHAu \rangle - \langle u | iAHu \rangle = -i \langle u | [A, H] u \rangle = 0 \quad //$$

Corollary: (Norm conservation)

If $\mathcal{M}$ contains rays, i.e. $u \in \mathcal{M} \Rightarrow \alpha u \in \mathcal{M}$ for $\alpha > 0$, then $\|u\|$ is conserved along variational approximations.

Proof: The stated condition implies $u \in T_u \mathcal{M}$. Hence, choose $A = I$ in the last theorem. //

Remark: Energy $\langle u | H | u \rangle$ is conserved if $Hu \in T_u \mathcal{M}$ (depends on specification of $\mathcal{M}$).

3.2.2 An a posteriori error bound

Theorem: If $u(0) = \psi(0) \in \mathcal{M}$, then the error of the variational approximation $u \in \mathcal{M}$ as compared to the exact wave function ψ is bounded by

$$\|u(t) - \psi(t)\| \le \int_0^t \operatorname{dist}\left(\tfrac{1}{i} H u(s), \mathcal{T}_{u(s)} \mathcal{M}\right) ds .$$

Proof: Let $P^\perp(u) = I - P(u)$, $P(u)$ ... ortho. proj. onto tangent space $\mathcal{T}_u \mathcal{M}$. Then

$$\frac{d}{dt}(u - \psi) = \frac{1}{i} H (u - \psi) - P^\perp(u) \frac{1}{i} H u \qquad \Big| \cdot (u - \psi)$$

$$\|u - \psi\| \frac{d}{dt} \|u - \psi\| = \frac{1}{2} \frac{d}{dt} \|u - \psi\|^2 = \operatorname{Re} \left\langle u - \psi \,\middle|\, \frac{d}{dt}(u - \psi) \right\rangle$$

$$= \operatorname{Re} \left\langle u - \psi \,\middle|\, - P^\perp(u) \frac{1}{i} H u \right\rangle \le \|u - \psi\| \, \|P^\perp(u) \tfrac{1}{i} H u\|$$

$$\Rightarrow \frac{d}{dt} \|u - \psi\| \le \|P^\perp(u) \tfrac{1}{i} H u\| .$$

Since $\operatorname{dist}\left(\tfrac{1}{i} H u, \mathcal{T}_u \mathcal{M}\right) = \|P^\perp(u) \tfrac{1}{i} H u\|$

$$\left(= \|\dot{u} - \tfrac{1}{i} H u\|\right)$$

$$\Rightarrow \frac{d}{dt} \|u - \psi\| \le \operatorname{dist}\left(\tfrac{1}{i} H u, \mathcal{T}_u \mathcal{M}\right) \qquad \Big| \int$$

$$\|u - \psi\| \le \int_0^t \operatorname{dist}\left(\tfrac{1}{i} H u(s), \mathcal{T}_{u(s)} \mathcal{M}\right) ds \qquad //$$

Remark: For the error of an observable A we conclude

$$|\langle u | A | u \rangle - \langle \psi | A | \psi \rangle| = |\langle u - \psi | A u \rangle + \langle A \psi | u - \psi \rangle|$$

$$\le \|u - \psi\| \left(\|A u\| + \|A \psi\| \right)$$

3.3 Adiabatic or Born/Oppenheimer approximation

Separation the motion of the heavy nuclei and light electrons! In this approach, the nuclear coordinates appear as fixed parameters!

Recall molecular Hamiltonian

$$H_{mol} = T_N + T_e + V, \quad V = V_{NN} + V_{Ne} + V_{ee},$$

$$T_N = -\sum_{n=1}^{N} \frac{1}{2M_n} \Delta_{x_n}, \quad T_e = -\sum_{e=1}^{L} \frac{1}{2} \Delta_{y_e},$$

$$V_{NN} = \sum_{1 \leq k < n \leq N} \frac{Z_k Z_n}{|x_k - x_n|}, \quad V_{Ne} = -\sum_{e=1}^{L} \sum_{n=1}^{N} \frac{Z_n}{|y_e - x_n|}, \quad V_{ee} = \sum_{1 \leq j < e \leq L} \frac{1}{|y_j - y_e|}$$

Motivated by the fact that $M_n >> 1$, we ignore the contribution from the kinetic energy of the nuclei, T_N, and consider the electronic Hamiltonian

$$H_e(x) = T_e + V(x, \cdot),$$

where now the nuclear coordinates x appear only as parameters.

Now consider the electronic structure problem

$$H_e(x)\, \Phi(x, \cdot) = E(x)\, \Phi(x, \cdot),$$

typically for the smallest eigenvalue E, the ground state energy.

We do not discuss the electronic structure problem here, but suppose that this problem is solved satisfactorily in some way!

Fix an eigenfunction $\Phi(x,\cdot)$ of $H_e(x)$ corresponding to the eigenvalue $E(x)$.

(in quantum chemistry, the eigenvalues are referred to as "bands")

Assume that $\Phi(x,y)$ depends smoothly on x, and $\|\Phi(x,\cdot)\| = 1$.

For fixed nuclear coordinates x, the solution of the time-dependent electronic Schrödinger equation

$$i\dot{\psi}_e = H_e(x)\psi_e, \quad \psi_e(0) = \psi_0(x)\Phi(x,\cdot)$$

is given by

$$\psi_e(x,y,t) = e^{-iE(x)t}\psi_0(x)\Phi(x,y).$$

Thus, we consider the adiabatic approximation to the molecular Schrödinger equation, i.e. the variational approximation on

$$\mathcal{M} = \{u \in L^2 : u(x,y) = \psi(x)\Phi(x,y),\ \psi \in L^2\}$$

Remark: $\mathcal{M}$ is a linear space, s.t. $T_u\mathcal{M} = \mathcal{M}$, $u \in \mathcal{M}$

We now derive a Schrödinger equation for the nuclei on the "electronic energy surface" given by the ground state E of the electronic structural problem:

For $u(x,y;t) = \Psi(x,t)\Phi(x,y)$ we have

$$T_N u = -\sum_{n=1}^{N} \frac{1}{2M_n}\left(\Delta_{x_n}\Psi\cdot\Phi + 2\nabla_{x_n}\Psi\bullet\nabla_{x_n}\Phi + \Psi\cdot\Delta_{x_n}\Phi\right)$$

Recall $\|\Phi(x,\cdot)\|^2_{L^2(y)} = 1\ \forall x$ and the variational principle

$$\langle v \,|\, i\dot{u} - Hu \rangle = 0 \quad \text{for } v = \varphi(x)\Phi(x,y),$$

$\varphi(x) \in L^2_x$ arbitrary.

We conclude

$$\Big\langle \varphi \,\Big|\, i\dot{\Psi} - E\Psi + \sum_{n=1}^{N}\frac{1}{2M_n}\Big(\Delta_{x_n}\Psi + 2\langle\nabla_{x_n}\Phi|\Phi\rangle_{L^2(y)}\nabla_{x_n}\Psi - \langle\nabla_{x_n}\Phi|\nabla_{x_n}\Phi\rangle_{L^2(y)}\Psi\Big)\Big\rangle_{L^2(x)} = 0$$

Since $2\operatorname{Re}\langle\nabla_{x_n}\Phi|\Phi\rangle_{L^2(y)} = \nabla_{x_n}\|\Phi\|^2_{L^2(y)} = 0$ (from $\|\Phi(x,\cdot)\|^2 = 1\ \forall x$)

we obtain

$$i\dot{\Psi} = H_N\Psi, \quad H_N = T_N + E + B_1 + B_2,$$

$$B_1 := \sum_{n=1}^{N}\frac{1}{M_n}\operatorname{Im}\langle\nabla_{x_n}\Phi|\Phi\rangle_{L^2(y)}\bullet p_n,$$

$$B_2 := \sum_{n=1}^{N}\frac{1}{2M_n}\|\nabla_{x_n}\Phi\|^2_{L^2(y)},$$

$$p_n := -i\nabla_{x_n}$$

$B_1, B_2 \ldots$ contain the reciprocals of the large nuclear masses, $\frac{1}{M_n}$, and are of lower differentiation order (only gradients are involved) than the kinetic energy terms $\Rightarrow$ these are neglected, and this yields the "time-dependent Born-Oppenheimer approximation"

$$i\dot{\Psi} = (T_N + E)\Psi =: H_{BO}\Psi.$$

3.4 Semiclassical Scaling

We rescale the molecular Schrödinger equation with the small parameter (assume $M_n \equiv M \; \forall n$)

$$\varepsilon^2 = \frac{m}{M} \ll 1.$$

This yields

$$i\dot{\Psi} = H^{\varepsilon}_{mol}\Psi,$$

$$H^{\varepsilon}_{mol} = -\frac{\varepsilon^2}{2}\Delta_x + H_e(x), \quad H_e(x) = -\frac{1}{2}\Delta_y - V(x,\cdot)$$

We are interested in solutions of bounded energy, particularly of bounded kinetic energy, i.e. Ψ s.t.

$$\langle \Psi | -\frac{\varepsilon^2}{2}\Delta_x | \Psi \rangle = \frac{1}{2}\|\varepsilon \nabla_x \Psi\|^2 = O(1) \qquad (*)$$

(the identity follows from integration by parts).

Consider a wave packet $e^{ip\cdot x} a(x)$ with momentum $p = Mv$.

The interpretation of p as an approximation to the momentum is shown as follows:

Consider a solution of the free Schrödinger equation

$$i\dot{\psi} = -\frac{1}{2M}\Delta\psi, \quad \psi(0) = e^{ip\cdot x} a(x),$$

with $a(x)$ a "well-behaved" Schwartz function, i.e. $a \in C^\infty$, a and all its derivatives decay faster than the inverse of any polynomial as $|x| \to \infty$.

Then the center of the wave packet

$$q(t) := \int_{\mathbb{R}^3} x\,|\psi(x,t)|^2\,dx$$

can be shown to move according to

$$q(t) \approx q(0) + t\,p/M$$

(i.e., $M\dot{q} \approx p$), see [14].

Thus, for a wave packet, the condition (*) from (36) corresponds to $p \sim 1/\varepsilon \Rightarrow v = p/M \sim \varepsilon$.

Consequently, motion over a distance ~ 1 takes place on a time scale $\sim 1/\varepsilon$.

These observations motivate to rescale time according to $t \leftarrow \frac{t}{\varepsilon}$

In this new time, nuclear motion over distances ~ 1 occurs over time ~ 1.

The molecular Schrödinger equation then reads

$$i\varepsilon \dot{\Psi} = H^{\varepsilon}_{mol} \Psi .$$

The equation for the nuclei becomes

$$\boxed{i\varepsilon \dot{\psi} = H^{\varepsilon}_{N} \psi}$$

$$H^{\varepsilon}_{N} := -\frac{\varepsilon^2}{2}\Delta_x + E + \varepsilon B_1 + \varepsilon^2 B_2 ,$$

$$B_1 := \mathrm{Im} \langle \nabla_x \Phi | \Phi \rangle_{L^2(y)} \cdot p , \; B_2 := \frac{1}{2} \| \nabla_x \Phi \|^2_{L^2(y)} +$$

$$p := -i\varepsilon \nabla_x .$$

We are interested in solutions over times $t = O(1)$.

<u>Error analysis for the Born-Oppenheimer approximation:</u>

Assume

1) Unbounded Coulomb potential is regularized s.t.

$$\| \nabla_x V(x,y) \| \le C_V \quad \forall x \in \mathbb{R}^{3N}, \; y \in \mathbb{R}^{3L}$$

2) Initial data on the manifold

$$\mathcal{M} = \{ u \in L^2(x,y) ; \; u = \psi(x) \Phi(x,y) , \; \psi \in L^2 \}$$

Recall: Φ ground state of electronic structure problem.

$\Psi_0(x,y) = \Psi_0(x)\,\Phi(x,y)$, with

$\|H_N^\varepsilon \Psi_0\| \le C_0, \quad \|\Psi_0\| = 1$ (1)

3) Spectral gap condition: For the ground state energy $E(x)$,

dist$\big(E(x), \sigma(H_e(x)) \setminus E(x)\big) \ge \delta > 0$.

Then the approximation u is defined by the variational principle (recall $\mathcal{M} = T_u\mathcal{M}$)

$\dot u \in \mathcal{M}$ s.t. $\langle v | \dot u - \frac{1}{i\varepsilon} H^\varepsilon_{mol}\, u \rangle = 0 \ \forall v \in \mathcal{M}$.

This satisfies the following "Space-Adiabatic Theorem":

Theorem: Under the assumptions 1) - 3), the error of the adiabatic approximation satisfies

$\|u(t,\cdot) - \Psi(t,\cdot)\|_{L^2} \le \mathcal{C}(1+t)\,\varepsilon, \quad t \ge 0,$

where $\mathcal{C}$ is independent of t, ε, and

initial data satisfying (1), but depends on δ, partial derivatives of Φ w.r.t. x up to third order, and on C_V and C_0 above.

Proof: [14].