Proof of Lemma 2:

Noting that the substeps with T, given by the flow of the free Schrödinger equation $e^{-i\Delta t T}$, are propagated by a unitary group of operators (due to the Theorem of Stone), we need to show

$$\| \varphi^t_{\hat{V}}(u_0) - \varphi^t_{\hat{V}}(v_0) \| \leq e^{\gamma t} \| u_0 - v_0 \|.$$

Writing $u(t) = \varphi^t_{\hat{V}}(u_0)$, $v(t) = \varphi^t_{\hat{V}}(v_0)$ and recalling $u = P(u)u$ and $v = P(v)v$, we have

$$\dot{u} - \dot{v} = -i P(u) V P(u)(u-v) -$$
$$- i [P(u) V P(u) - P(v) V P(v)] v. \quad | \cdot (u-v)$$

$$\|u-v\| \frac{d}{dt} \|u-v\| = \operatorname{Re} \langle u-v | \dot{u} - \dot{v} \rangle =$$
$$= \operatorname{Re} \langle u-v | -i [P(u) V P(u) - P(v) V P(v)] v \rangle =$$
$$= \operatorname{Im} \langle u-v | P(u) V (P(u) - P(v)) v \rangle +$$
$$+ \operatorname{Im} \langle u-v | [P(u) - P(v)] P(v) V v \rangle +$$
$$+ \operatorname{Im} \langle u-v | [P(u) - P(v)] P^\perp(v) V v \rangle = I + II + III$$

To bound I, we write

$$[P(u) - P(v)] v = -[P^\perp(u) - P^\perp(v)] v = -P^\perp(u) v =$$
$$= P^\perp(u)(u-v).$$

(2) from p. 58 thus gives $|I| \leq \beta \varkappa \|u-v\|^3$

For estimating II, we write

$$\langle u-v \,|\, [P(u)-P(v)]\,P(v)V_v \rangle =$$

$$= -\langle u-v \,|\, [P^\perp(u)-P^\perp(v)]\,P(v)V_v \rangle =$$

$$= -\langle u-v \,|\, P^\perp(u)P(v)V_v \rangle =$$

$$= -\langle P^\perp(u)(u-v) \,|\, P^\perp(u)P(v)V_v \rangle =$$

$$= \langle P^\perp(u)(u-v) \,|\, [P(u)-P(v)]\,P(v)V_v \rangle .$$

With (1)-(2) on p. 58 it follows

$$|II| \le \beta \varkappa^2 \|u-v\|^3 .$$

Finally, from

$$\|P^\perp(v)V_v\| = \mathrm{dist}(V_v, T_v M) = \delta + O(\Delta t)$$

and (1) on p. 58 we have

$$|\underline{III}| \le \varkappa(\delta + O(\Delta t))\|u-v\|^2 .$$

Thus, as long as $\|u-v\| = O(\Delta t)$, we obtain

$$\frac{d}{dt}\|u-v\| \le (\varkappa\delta + O(\Delta t))\|u-v\| . \ //$$

3.5 Gaussian Wavepacket Dynamics

To descend one step further in the complexity of model reductions, we parametrize the approximation by a finite number of parameters.

For the Schrödinger equation in semi-classical scaling (cf. the Born-Oppenheimer approximation on p. 38)

$$i\varepsilon \dot{\psi} = -\frac{\varepsilon^2}{2}\Delta\psi + V\psi, \quad \varepsilon \ll 1$$

we seek an approximation in the form of a Gaussian wavepacket

$$\psi \approx u = \exp\left(\frac{i}{\varepsilon}\left[(x-q(t))^T C(t)(x-q(t)) + p(t)\cdot(x-q(t)) + \zeta(t)\right]\right)$$

$C(t)$ is a complex symmetric matrix with positive definite imaginary part, $\zeta \in \mathbb{C}$ is a phase, $q(t)$ is a position average, $p(t)$ is a momentum average.

This ansatz was proposed in [39]. Therein, equations of motion for the parameters were derived,

$$\dot{q} = p$$

$$\dot{p} = -\langle u | \nabla V | u \rangle$$

$$\dot{C} = -2C^2 - \frac{1}{2}\langle u | \nabla^2 V | u \rangle$$

$$\dot{\zeta} = \frac{1}{2}|p|^2 - \langle V \rangle + i\varepsilon\, \mathrm{tr}(C) + \ldots$$

$$+ \frac{\varepsilon}{8}\langle u | \mathrm{tr}((\mathrm{Im}(C))^{-1}\nabla^2 V) | u \rangle.$$

<u>Remark</u>: Note that as $\varepsilon \to 0$, the ansatz function u becomes increasingly narrow, whence $\langle u|\nabla V|u\rangle \to \nabla V(q)$. Thus the equns for q & p become the classical Newtonian dynamics (see p. 1)

$$\dot{q} = p, \ \dot{p} = -\nabla V(q).$$

<u>Theorem</u> (without proof): Consider a variational approximation by Gaussian wave packets from p. 65. Assume that the smallest eigenvalue of $\mathrm{Im}(C(t))$ is bounded from below by a constant $\rho > 0$. Assume $V \in C^3$. Then for coincident Gaussian initial data,

$$\|u(t) - \psi(t)\| \le C \cdot t\, \varepsilon^{1/2},$$

where $C = C(\rho, \|\partial^3 V\|)$. <u>Proof</u>: [14]

<u>Numerical Approximation</u> (due to [5])

Variational splitting yields the following subproblems:

1.) Substep with V:

$$\dot{q} = 0, \ \dot{p} = -\langle u|\nabla V|u\rangle, \ \dot{C} = -\tfrac{1}{2}\langle u|\nabla^2 V|u\rangle,$$

$$\dot{\zeta} = -\langle u|V|u\rangle + \tfrac{\varepsilon}{8}\langle u|\mathrm{tr}((\mathrm{Im}\, C)^{-1}\nabla^2 V)|u\rangle$$

2.) Substep with T:

$$\dot{q} = p, \ \dot{p} = 0, \ \dot{C} = -2C^2, \ \dot{\zeta} = \tfrac{1}{2}|p|^2 + i\varepsilon\, \mathrm{tr}(C).$$

Remarkably, all the substeps in the above algorithm admit an explicit solution:

1) $q(t) = q^0$, $p(t) = p^0 - t\langle u|\nabla V|u\rangle^0$,

$C(t) = C^0 - \frac{t}{2}\langle u|\nabla^2 V|u\rangle^0$,

$\zeta(t) = \zeta^0 - t\langle u|V|u\rangle^0 + \frac{t\varepsilon}{8}\langle u|\mathrm{tr}((\mathrm{Im}\, C^0)^{-1}\nabla^2 V)\rangle^0$

2) $q(t) = q^0 + tp^0$, $p(t) = p^0$, $C(t) = C^0(I + 2tC^0)^{-1}$,

$\zeta(t) = \zeta^0 + \frac{t}{2}|p^0|^2 + \frac{i\varepsilon}{2}\mathrm{tr}\left(\log(I + 2tC^0)\right)$.

This results in the following algorithm [5]:

<u>Algorithm</u>: For $W = V, \nabla V, \nabla^2 V$, write $\langle W\rangle^n = \langle u^n|W|u^n\rangle$.

Starting from the Gaussian u^n with parameters q^n, p^n, C^n, ζ^n, a time step of the Gaussian wave packet variational integrator $u^n \mapsto u^{n+1}$, $t^n \mapsto t^n + \Delta t$, is performed as follows:

1) $p^{n+1/2} = p^n - \frac{\Delta t}{2}\langle \nabla V\rangle^n$

$C_+^n = C^n - \frac{\Delta t}{4}\langle \nabla^2 V\rangle^n$

$\zeta_+^n = \zeta^n - \frac{\Delta t}{2}\langle V\rangle^n + \frac{\Delta t\,\varepsilon}{16}\langle \mathrm{tr}((\mathrm{Im}\, C^n)^{-1}\nabla^2 V)\rangle^n$

2) $q^{n+1} = q^n - \Delta t\, p^{n+1/2}$

$C_-^{n+1} = C_+^n (I + 2\Delta t\, C_+^n)^{-1}$

$\zeta_-^{n+1} = \zeta_+^n + \frac{\Delta t}{2} |p^{n+1/2}|^2 + \frac{i\varepsilon}{2} \mathrm{tr}(\log(I + 2\Delta t\, C_+^n))$

3) Noting that the averages below are the same as those for $q^{n+1}, C_-^{n+1}, \zeta_-^{n+1}$,

$p^{n+1} = p^{n+1/2} - \frac{\Delta t}{2} \langle \nabla V \rangle^{n+1}$

$C^{n+1} = C_-^{n+1} - \frac{\Delta t}{4} \langle \nabla^2 V \rangle^{n+1}$

$\zeta^{n+1} = \zeta_-^{n+1} - \frac{\Delta t}{2} \langle V \rangle^{n+1} + \frac{\Delta t\, \varepsilon}{16} \langle \mathrm{tr}((\mathrm{Im}\, C^{n+1})^{-1} \nabla^2 V) \rangle^{n+1}.$

The method is of second order,

and has nice "geometric properties":

1) Preserves unit L^2 norm.

2) Time-Reversible.

3) "Symplectic", see [8].

Proof: [14].

3.6 Time-Dependent Density Functional Theory

To reduce the complexity further, linear scaling w.r.t. the degrees of freedom (# particles) can be achieved by the decoupling of <u>Density Functional Theory</u> [35, 36].

This is based on the <u>Hohenberg-Kohn Theorem</u> [35].

<u>Theorem</u>: Let Ψ_0 denote the ground state (eigen function to lowest eigenvalue of Hamiltonian H). This is assumed to be non-degenerate, i.e., the associated subspace has dimension 1. Let

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$$

be the ground state energy. The electron density is

$$\rho(x) = f\langle \Psi | \Psi \rangle^{(\neg x)} =$$

$$= f \int_{\mathbb{R}^3} \cdots \int_{\mathbb{R}^3} \overline{\Psi}(x, x_2, \dots, x_f)\, \Psi(x, x_2, \dots, x_f)\, dx_2 \cdots dx_f .$$

Then E_0 is a functional of ρ, $E_0 = E_0(\rho)$.

<u>Proof</u>: [35, 23].

The time-dependent version given in the following was proven in [37], see also [2, 15].

Consider

$$i\dot{\Psi} = H\Psi, \quad H = -\frac{1}{2}\sum_{k=1}^{f}\Delta^{(k)} + \frac{1}{2}\sum_{k=1}^{f}\sum_{j\neq k}\frac{1}{|x_k - x_j|} + V_{ext}(x,t) \quad (1)$$

where the separable part of the potential, V_{ext}, may comprise e.g. nuclear attraction or other external fields such as a laser field,

$$V_{ext}(x,t) = \sum_{k=1}^{f} v_{ext}(x_k, t).$$

<u>Theorem ([37])</u>: Consider the time-evolution of (1) for two external potentials which differ by more than a constant,

$$v_{ext}(x,t) - \tilde{v}_{ext}(x,t) \neq c(t),$$

with $\tilde{\Psi}(x,0) = \Psi(x,0)$.

Then there is $t^* > 0$ s.t. for the associated densities

$$\rho(x,t^*) \neq \tilde{\rho}(x,t^*).$$

Under these conditions, there is a one-to-one mapping between densities and potentials, or in other words, the external potential is a functional of the density.