A review of the time-dependent variational principle

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Abstract. The time-dependent variational principle associates to a Hamiltonian quantum system a set of trajectories running on a classical phase space $\mathcal{M}$ with canonical equations of motion. When the quantum observables generate a Lie group $G$ and the states are taken as functions on an appropriate homogeneous quotient space $\mathcal{M} := G/G_0$ under $G$, they can be equipped with a classical Poisson bracket which reproduces the commutators of the Lie group. The quantum system maps into a classical system whose equations of motion are governed by the expectation value $\mathcal{H}$ of the quantum Hamiltonian $H$. We consider examples of this construction and show that the analysis of generalized classical systems provides insight into quantum many-body dynamics like chemical reactions.

1. The time-dependent variational principle
For a general review on variational principles in quantum mechanics we refer to [1] and [2]. Specifically we shall work with a time-dependent variational principle described in [3].

Consider a state space, a quantum Hamiltonian $H$, and the variational principle

$$|\psi\rangle = |\psi(x,t)\rangle, \quad \delta S = 0, \quad S = \int_{t_1}^{t_2} L(\psi, \overline{\psi}) dt, \quad (1)$$

$$L(\psi, \overline{\psi}) = \frac{i}{2} \frac{\langle \psi|\dot{\psi}\rangle - \langle \dot{\psi}|\psi\rangle}{\langle \psi|\psi\rangle} - \frac{\langle \psi|H|\psi\rangle}{\langle \psi|\psi\rangle}.$$ 

It is shown in [3] pp. 3-5 that the variational principle eq. 1 yields the time-dependent Schrödinger equation. Among other variational principles this one has the property [3] p. 4 that its solutions $\psi$ are independent of a scaling with any complex factor,

$$\psi(x,t) \Rightarrow \tilde{\psi}(x,t) = \psi(x,t) f(t). \quad (2)$$

This independence is needed for use with analytic but not normalized coherent states.

2. Variational solutions with trajectories
Choose functions $\psi$ of general coordinates $x = (x_1, x_2, ..., x_N)$ on a manifold $\mathcal{M}$ of dimension $N$, introduce trajectories $x_1(t), x_2(t), ..., x_N(t)$ on $\mathcal{M}$, and consider $\psi$ as a function of these trajectories,

$$|\psi(x_1, \ldots, x_N, t)\rangle \Rightarrow |\psi(x_1(t), \ldots, x_N(t))\rangle. \quad (3)$$
The Lagrangian becomes

\[ L = \sum_1^N \dot{x}_j Z_j - \mathcal{H}, \quad (4) \]

\[ Z_j(x) := \frac{i}{2} \frac{1}{\langle \psi | \psi \rangle} \left[ \langle \psi | \partial \psi \partial x_j \rangle \right] - \langle \partial \psi \partial x_j | \psi \rangle \]

\[ H(x) := \langle \psi | H | \psi \rangle \langle \psi | \psi \rangle. \]

The equations of motion with an antisymmetric tensor \( \eta \) become

\[ \delta S = 0 \Rightarrow \tag{5} \]

\[ \sum_j \eta_{ij}(x) \dot{x}_j = \frac{\partial \mathcal{H}}{\partial x_i}, \]

\[ \eta_{ij}(x) := \frac{\partial Z_j}{\partial x_i} - \frac{\partial Z_i}{\partial x_j}. \]

These are equations of motion for the trajectories. \( \eta \) contains the 2nd partial derivatives of the overlaps between the states and gives some kinematics. The function \( \mathcal{H}(x) \) yields the dynamics in these equations.

Let us assume that \( \eta \) taken as a matrix has a well-defined inverse. The inversion of \( \eta \) allows to introduce a Poisson bracket \( \mathcal{PB} \) on \( \mathcal{M} \), taken as a phase space. Technically one must check for these brackets the Jacobi identity and similar properties, see [3] pp. 10-11 for details. Once these are verified, the TDVP can be called a dequantization of the system and its observables in the following sense:

Quantum operator \( A \) \( \Rightarrow \) Expectation value \( A \) on \( \mathcal{M} \),
Commutator \([A, B] \) \( \Rightarrow \) Poisson bracket \([A, B]_{\mathcal{PB}} \),
Heisenberg Quantum \( \Rightarrow \) General Poisson Dynamics.

3. From quantum observables to Lie groups

If the quantum observables generate a Lie group \( G \) with coherent states \( CS \), the manifold \( \mathcal{M} \) and the \( PBs \) from the TDVP link up with group representations via Geometric quantization. We cannot go into this theory and instead prefer to proceed by examples. Our principal example are the familiar angular momentum observables, the rotation group \( SU(2) \) (including spin), and corresponding coherent states.

4. Rotational coherent states and Poisson brackets for \( SU(2) \)

Consider the operators \( J_1, J_2, J_3 \) of angular momentum with their familiar commutation relations, the Lie group \( SU(2) \) generated by them, and the state space spanned by the states

\[ |jm \rangle, \quad -j \leq m \leq j, \quad j = 0, 1/2, 1, 3/2, ... \quad (7) \]

The extremal state \( |jj \rangle \) is stable under rotations \( V_3(\alpha) \) around the 3-axis. These operators form the subgroup \( G_0 \sim U(1) \) of rotations around the 3-axis. The rotational coherent states \( CS \) in terms of Euler angles \((\alpha\beta\gamma)\), corresponding rotation operators \( V(\gamma \beta \alpha) = V_3(\gamma)V_2(\beta)V_3(\alpha) \), and their overlap \((\alpha \rightarrow 0)\) are defined by

\[ |\beta \gamma \rangle := V(\gamma \beta 0)|jj \rangle. \quad (8) \]
The two coordinates $\beta, \gamma$ parametrize a sphere $M = S^2$, which as a manifold is the homogeneous quotient space $SU(2)/U(1)$. The overlap between two coherent states can be computed as

$$\langle \beta'\gamma' | \beta\gamma \rangle = \left[ \cos\left(\frac{\beta'}{2}\right) \cos\left(\frac{\beta}{2}\right) \exp\left(i(\frac{\gamma'}{2} - \frac{\gamma}{2})\right) + \sin\left(\frac{\beta'}{2}\right) \sin\left(\frac{\beta}{2}\right) \exp\left(-i(\frac{\gamma'}{2} - \frac{\gamma}{2})\right) \right]^{2j}.$$  

We define the classical angular momentum observables as the expectation values of the quantum operators between coherent states and obtain

$$J_1 = \langle \beta\gamma | J_1 | \beta\gamma \rangle = j \sin(\beta) \cos(\gamma),$$
$$J_2 = \langle \beta\gamma | J_2 | \beta\gamma \rangle = j \sin(\beta) \sin(\gamma),$$
$$J_3 = \langle \beta\gamma | J_3 | \beta\gamma \rangle = j \cos(\beta).$$

We now wish to show that $M = S^2$ qualifies as a phase space for $SU(2)$. Actually this phase space is just Euler’s angular momentum $J$-sphere but from eq. 10 has the quantum radius $j$.

To see its Poisson structure we define a Poisson bracket for functions $F, G$ on $S^2$:

$$[F, G]_{PB} := \frac{i}{j \sin(\beta)} \left[ \frac{\partial F}{\partial \beta} \frac{\partial G}{\partial \gamma} - \frac{\partial F}{\partial \gamma} \frac{\partial G}{\partial \beta} \right].$$

These Poisson brackets eq. 11, taken for the classical angular momentum observables $J_i$ eq. 10, reproduce the quantum commutators, that is,

$$[J_1, J_2] = iJ_3 \Rightarrow [J_1, J_2]_{PB} = iJ_3.$$  

Consider now a quantum Hamiltonian $H$ which is a function of the angular momentum operators. The classical equations of motion for the angular momentum observables are then given by the equations

$$\dot{J}_i = [H, J_i]_{PB}.$$  

Moreover the classical Hamiltonian is conserved under these equations of motion. It follows that for fixed energy and angular momentum the dynamics runs on the intersection of the Hamiltonian $E$-surface and Euler’s angular momentum $J$-sphere. We refer to Arnold [4] pp. 323-7.

A classical example is provided by a rigid top. The energy $E$-ellipsoid, with axes determined by three moments of inertia, intersects with the Euler $J$-sphere. Since both quantities are conserved, the dynamics must run on the intersection. A second example coming from quantum dynamics is the Lipkin model for fermions in two levels [3] pp.53-62. This model has an illuminating classical version on the angular momentum sphere.

5. Coherent states and the TDVP yield Poisson brackets from a Lie group $G$

We sketch [3] pp. 15-28 how the scheme just outlined generalizes to a general Lie group. First of all we require a generalized extremal state $|jj\rangle \Rightarrow |0\rangle$, stable under the operations of a subgroup $G_0 < G$.

Next we factorize any group element $g$ modulo the subgroup $G_0$ as $g = c g_0$, $g_0 \in G_0$, where now $c \in M = G/G_0$.

Then we apply the group operators $V(c)$ to the extremal state and in this way determine coherent states $CS$,

$$CS : |\psi(c)\rangle := V(c)|0\rangle.$$  

The Poisson bracket in general is determined by the derivatives of coherent state overlaps $\langle \psi(c')|\psi(c)\rangle$. 

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The **Classical observables** are defined as the expectation values of operators between coherent states, \( B \Rightarrow \mathcal{B} = \langle \psi(c) | B | \psi(c) \rangle \).

The Lie generators as expectation values \( A_i \Rightarrow A_i \) map into functions on \( \mathcal{M} \).

The construction assures that the Poisson brackets of the classical generators reproduce the commutators of the group \( G \),

\[
[A_i, A_j] = \sum_k c_{ij}^k A_k \Rightarrow [A_i, A_j]_{PB} = \sum_k c_{ij}^k A_k.
\] (15)

**Remark 1:** Generalized Moyal brackets: The relation eq. 15 is valid only for operators linear in the Lie algebra. If we start from polynomials in the quantum generators, their transcription into classical operators requires the construction of a Moyal bracket, see [3] pp. 43-45.

**Remark 2:** Stability groups: We add that, for a given Lie group \( G \), the choice of the subgroup \( G_0 \) is not arbitrary. To describe the possible subgroups one needs the concept of the action by conjugation \( G \times G \rightarrow G \) defined by the homomorphic map

\[
G \times G \rightarrow G, \ g \in G, g' \in G, \ (g, g') \rightarrow gg'g^{-1}.
\] (16)

Under this action (as under any homomorphic action), the Lie group \( G \) decomposes into orbits. These orbits for the action eq. 16 are nothing but the familiar classes of the group. If in eq. 16 we pass from the second copy of \( G \) to its Lie algebra, we arrive at the so-called adjoint action, see [4] pp. 318-42. For any such class or orbit, there is a stability group which conjugates a chosen representative of the class into itself. Now we can state, [3] pp. 15-28, for a compact Lie group \( G \) the candidates \( G_0 \) for the construction of a Poisson bracket as described above: \( G_0 \) must be the stability group of some class of \( G \), or must belong to an adjoint orbit. The adjoint action for a compact Lie group is dual to the coadjoint action which is studied in the theory of geometric quantization. More information on geometric quantization and Lie groups can be found in [5].

For the example of \( SU(2) \), the adjoint action eq.16 transforms the generators of the group as a vector. Its stability group can be taken as the subgroup of rotations around the 3-axis.

In what follows we shall concentrate on coherent states for observables which allow to describe the dynamics of present-day chemical reactions, and then report on a detailed application.

6. **Boson coherent states (Glauber, Bargmann)**

The familiar treatment of harmonic oscillators uses a finite set of annihilation and creation operators \( A_j, A_j^\dagger \) with standard commutation properties. A similar but denumerable set of operators is used in the field quantization of infinite boson systems. The annihilation and creation operators generate the Heisenberg-Weyl group \( G \). An extremal (ground) state \( |0\rangle \) is characterized by

\[
|0\rangle : A_j |0\rangle = 0, \ j = 1, 2, ...
\] (17)

Glauber [6] 1963 and later Bargmann [7] 1968 introduced and analyzed analytic coherent states \( CS \) and their overlap for the Heisenberg-Weyl group in terms of complex variables \( z = (z_i) \) and their overlap:

\[
|z\rangle := \exp(\sum_i z_i A_i^\dagger)|0\rangle,
\] (18)

\[
\langle z'|z\rangle = \exp(\sum_i z_i z_i^\dagger).
\]

Bargmann [7] developed a Hilbert space of functions analytic in the complex variables \( z \) and its map to the standard Hilbert space of quantum mechanics. In his analysis the overlap in eq.
18 becomes the reproducing kernel in the Hilbert space and replaces the Dirac $\delta$-distribution of the Schrödinger representation. Using the coherent states eq.18 we can define and compute Classical creation/annihilation observables as expectation values:

$$A_i^\dagger = z_i, \quad A_j = \bar{z}_j.$$  \hspace{1cm} (19)

All classical observables taken as expectation values will be functions of $(z, \bar{z})$. The Poisson brackets for two functions $F(z, \bar{z}), G(z, \bar{z})$ constructed in [3] pp. 41-2 are:

$$[F, G]_{PB} = \sum_i \left[ \frac{\partial F}{\partial z_i} \frac{\partial G}{\partial \bar{z}_i} - \frac{\partial F}{\partial \bar{z}_i} \frac{\partial G}{\partial z_i} \right].$$  \hspace{1cm} (20)

These Poisson brackets turn out to be a complex form of the canonical fundamental Poisson brackets of classical mechanics. It can now easily be verified that the classical annihilation and creation operators eq.19, inserted into the Poisson brackets eq.20, reproduce the commutation properties of the quantum operators. Examples of applications for the coherent states are systems of bosons, quantum optics, and molecular vibrations to be discussed later.

7. Coherent states for fermions (Thouless)
The operator treatment of fermion systems uses anticommuting fermion creation and annihilation operators $(c_i^\dagger, c_i), i = 1...N$. A typical ground state corresponding to a Slater determinant is then given by

$$|\psi_0\rangle = \prod_{i=1}^{N} c_i^\dagger |0\rangle.$$  \hspace{1cm} (21)

We shall take a state of this type as an extremal state. We augment the $N$ pairs of fermion creation and annihilation operators for $N$ occupied states by a set of similar operators $(c_m^\dagger, c_m)$, $m = N+1, \ldots, M$ for $M-N$ unoccupied states. Particle-hole operators are defined by

$$C_{mi} := c_m^\dagger c_i.$$  \hspace{1cm} (22)

These operators can be shown to generate the unitary group $G = U(M)$. For the construction of fermion coherent states we follow Thouless [8] (1960) and construct excited single-determinant states by

$$|z\rangle := \exp(\sum_{i,m} z_{im} C_{mi}) |\psi_0\rangle,$$  \hspace{1cm} (23)

in terms of $N \times (N-M)$ complex variables $(z_{im})$. The overlap is found to be

$$\langle z'|z \rangle = \det(I_N + z'z^\dagger).$$  \hspace{1cm} (24)

An example for the application of these fermion coherent states is the time-dependent Hartree-Fock theory in nuclear physics [3], pp.71-76 with Poisson brackets constructed in [3] p. 75. Applications to chemical reactions will be discussed in the next sections.

8. The reaction Proton-Acetylene
Experimental studies by C P Toennies et al. 1987-89 reported on the following reactions:

\[ H^+ + (H - C \equiv C - H) \]
\[ \Rightarrow \text{NTS} : \quad H^+ + (H - C \equiv C - H), \]
\[ \Rightarrow \text{CTS} : \quad H^0 + (H - C \equiv C - H^+), \]
\[ \Rightarrow C - \text{HD} : \quad H^q + H^q' + (C \equiv C - H^q')(\nu_f, l_f), \]
\[ \Rightarrow C - \text{CD} : \quad H^q + (C - H^q') + (C - H^q'), \quad q + q' + q'' = 1, \]
\[ \Rightarrow \text{HR} : \quad H^* + (H - C \equiv C - H^*)(\nu_f, l_f). \]
The reaction channels will be denoted as:

- **NTS**: Non-Transfer Scattering
- **CTS**: Charge Transfer Scattering
- **C-HD**: collision-induced Carbon-Hydrogen Dissociation
- **C-CD**: collision-induced Carbon-Carbon Dissociation
- **HR**: Hydrogen H∗ Rearrangement

Vibrational+rotational final excitations will be denoted as $\nu_f, l_f$.

9. **State analysis of the nuclear part**

The theoretical analysis was developed by Morales et al., in [9] and called electron-nucleon dynamics (END). The nuclear part of the total state is taken as

$$\psi_{Nucl}(X; R, P) = \prod_{j=1}^{3N} \exp \left[ -\left( \frac{X_j - R_j}{\Delta R_j} \right)^2 + \frac{i P_j}{\hbar} (X_j - R_j) \right].$$

Used here are so-called frozen narrow Gaussian wave packets, as they were introduced by Heller [10], with average positions and momenta $R_j, P_j$. Morales [12] has described a state transcription of the type

$$\psi_{Nucl} \Rightarrow \psi_{Trans} \psi_{Rot} \psi_{Vib}.$$  

Here $\psi_{Trans}$ is a coherent state wave packet for the nuclear motions, $\psi_{Rot} = |\alpha, \beta\rangle$ is a rotational coherent state due to Morales, and $\psi_{Vib} = \prod_{i=1}^{N-6} |z_i\rangle$ is a Glauber-Bargmann vibrational coherent state.

10. **State analysis of the electron part**

The ground state of the system is taken as a fermionic single determinant

$$|\psi_{el,0}\rangle = c^\dagger_{el,1} \ldots c^\dagger_{el,3}|0\rangle,$$

built from electronic Molecular Spin-Orbitals or MSO. Here the electron creation operators refer to the nuclear centers $(R_j)$. The dynamical electron state is taken from eq. 23 as

$$\psi_{el}(\mu, R) = \exp \left[ \sum_{(p,h)} \mu_{ph} c^\dagger_p c_h \right] |\psi_{el,0}\rangle.$$ 

Here the exponential operator creates by particle-hole operators $c^\dagger_p c_h$ a Thouless excited single-determinant MSO wrt. the nuclear centers $(R_j)$. Charge transfer is explicitly included in the analysis.

11. **The TDVP equations of motion**

The total state of the system is introduced as

$$\psi_{Total} = \psi_{Nucl} \psi_{el}$$

into the TDVP. As the observables of the chemical reaction one takes the nuclear centers $\mathbf{R} = (R_1, R_2, R_3) =: \mathbf{R}(t)$, the momenta $\mathbf{P}(t)$, and electronic complex parameters $\mu_{ph} =: \mu_{ph}(t)$.
Figure 1. Initial data for the computation [9] of the reaction of a proton on acetylene. $H^+$ incoming in the $(x, z)$-plane with momentum $P$ and impact parameter $b$, target $H - C - C - H$ centered at $(0, 0, 0)$ with orientation $(\alpha, \beta)$.

The equations of motion become

$$
\begin{bmatrix}
  iC & 0 & iC_R & 0 \\
  0 & -i\bar{C} & -i\bar{C}_R & 0 \\
  iC_R^\dagger & -iC_R^T & C_{RR} & -1 \\
  0 & 0 & 1 & 0
\end{bmatrix}
\begin{bmatrix}
  \dot{\mu} \\
  \dot{\bar{\mu}} \\
  \dot{R} \\
  \dot{P}
\end{bmatrix}
= \begin{bmatrix}
  \partial_{\pi}\mathcal{H} \\
  \partial_{\bar{\mu}}\mathcal{H} \\
  \partial_{R}\mathcal{H} \\
  \partial_{P}\mathcal{H}
\end{bmatrix}.
$$

(31)

The blocks of the complex matrix $C$, equivalent to the tensor $\eta$ eq. 5 of the TDVP, are second derivatives of overlaps. The classical Hamiltonian becomes

$$
\mathcal{H} = \sum_i \frac{P_i^2}{2M_i} + \langle \mu, R | \mu, R \rangle^{-1} \langle \mu, R | H_{el} | \mu, R \rangle.
$$

(32)

The equations of motion eq. 31 are then solved for initial conditions according to Fig. 1 with projectile and target in the ground state. These initial conditions can be varied to find the variety of reaction channels. The TDVP reaction dynamics described in this way goes beyond the Born-Oppenheimer approximation. This can be seen by observing that the blocks $C_R$ in eq. 31 contain a coupling of electronic and nuclear dynamics in the form

$$
C_R \Rightarrow C_{\mu \phi, R_j} = -2\text{Im} \frac{\partial^2 \ln \langle \mu', R' | \mu R \rangle}{\partial \mu \phi \partial R_j} \bigg|_{R' = R, \mu' = \mu}.
$$

(33)

In passing we remark that Li Che et al. in [11] (2007) have demonstrated the break-down of the Born-Oppenheimer approximation in the reaction $F + $ortho-$D_2 \rightarrow DF + D$. 

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The initial state is taken as a proton $H^+$ starting with energy $E = 30\text{ eV}$ and impact parameter $b$ in the $(x,z)$ plane, whereas the linear target molecule ($HC - CH$) is centered at the origin with orientation $(\alpha, \beta)$. The final state shows well-separated molecular reaction channels. The total reaction amplitude factorizes as

$$S_{SC}^{i \rightarrow f} = A_{\text{Trans}}^{i \rightarrow f} A_{\text{Rot}}^{i \rightarrow f} A_{\text{Vib}}^{i \rightarrow f} A_{\text{el}}^{i \rightarrow f}. \tag{34}$$

The initial positions are schematically shown in Fig. 1.

The detailed results of the reaction dynamics can be found in Figures 1-5 in Morales et al. [9]. Their Fig. 2 displays various reaction channels and excitations found as functions of the impact parameter $b$ and target orientation $(\alpha, \beta)$. Their Fig. 3 shows the computed trajectories for $H_2$ formation. Their Fig. 5 gives the computed total differential cross section as a function of the scattering angle $\theta$, $0 \leq \theta \leq 20$ degrees. This computed cross section gives a very reasonable account of the experiment.

12. Conclusion

We can draw the following conclusions on the use of the TDVP from the detailed computation of a chemical reaction:

The time-dependent variational principle with coherent states carries a present-day complex quantum dynamics into a generalized classical dynamics. Boson and fermion quantum observables are mapped into trajectories on a quantum-based phase space $\mathcal{M}$. By solving the equations of motion for this generalized classical dynamics one can determine quantum transition probabilities for complex reaction channels.

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