

# Computational Methods for Correlated Quantum Systems

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## Abstract

Twelve lectures are presented for an overview of the theory and application of practical methods to describe equilibrium and nonequilibrium properties of correlated quantum systems. The first two lectures are presented by Dufty; the remaining ten lectures will be presented by Bonitz, Filinov, and Balzer by teleconference.

# Lectures 1,2 : Quantum potentials for semi-classical methods

## I. OVERVIEW OF QUANTUM STATISTICAL MECHANICS AND THE CLASSICAL LIMIT

### A. Quantum

Key ingredients: observables (Hermitian operators  $\{A\}$ ), states (normalized positive Hermitian operators  $\{\rho\}$ ), Hamiltonian dynamics. Formulated in an  $N$  particle Hilbert space  
Expectation values

$$\langle A; \rho \rangle = \text{Tr} A \rho, \quad A^\dagger = A, \quad \text{Tr} \rho = 1. \quad (1)$$

Dynamics

$$\langle A(t); \rho \rangle = \text{Tr} A(t) \rho = \text{Tr} A \rho(t), \quad A(t) = e^{Lt} A, \quad \rho(t) = e^{-Lt} \rho \quad (2)$$

$$LX = \frac{i}{\hbar} [H, X] \quad (3)$$

### B. Classical

Key ingredients: observables (real phase functions  $\{A\}$ ), states (normalized, phase functions  $\{\rho\}$ ), Hamiltonian dynamics. Formulated in an  $N$  particle phase space ( $\Gamma \equiv \{\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N\}$ )  
Expectation values

$$\langle A; \rho \rangle = \int d\Gamma A(\Gamma) \rho(\Gamma), \quad A^+ = A, \quad \int d\Gamma \rho(\Gamma) = 1 \quad (4)$$

Dynamics

$$\langle A(t); \rho \rangle = \int d\Gamma A(\Gamma_t) \rho(\Gamma) = \int d\Gamma A(\Gamma) \rho(\Gamma_{-t}), \quad A(t) = e^{Lt} A, \quad \rho(t) = e^{-Lt} A \quad (5)$$

$$LX = \{H, X\} = \sum_{i=1}^N \left( \frac{\partial H}{\partial \mathbf{q}_i} \cdot \frac{\partial X}{\partial \mathbf{p}_i} - \frac{\partial H}{\partial \mathbf{p}_i} \cdot \frac{\partial X}{\partial \mathbf{q}_i} \right) \quad (6)$$

### C. Classical as limit of quantum: Canonical partition function

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j=1}^N V(|\mathbf{q}_i - \mathbf{q}_j|) = K + V \quad (7)$$

$$\begin{aligned} Q_N &= \text{Tr} e^{-\beta H_N} = \sum_{\alpha_1} \dots \sum_{\alpha_n} \langle \alpha_1, \dots, \alpha_N | e^{-\beta H} \mathcal{S} | \alpha_1, \dots, \alpha_N \rangle \\ &= \sum_{\alpha_1} \dots \sum_{\alpha_n} \langle \alpha_1, \dots, \alpha_N | e^{-\beta H} \frac{1}{N!} \left( 1 + \frac{1}{2} \sum_{i,j=1}^N (\pm \mathcal{P}_{ij}) + \dots \right) | \alpha_1, \dots, \alpha_N \rangle \\ &= \int d\mathbf{q}_1 \dots d\mathbf{q}_N \sum_{\mathbf{p}_1} \dots \sum_{\mathbf{p}_N} \langle \mathbf{q}_1 \dots \mathbf{q}_N || \mathbf{p}_1 \dots \mathbf{p}_N \rangle \langle \mathbf{p}_1 \dots \mathbf{p}_N | e^{-\beta H} \mathcal{S} | \mathbf{q}_1 \dots \mathbf{q}_N \rangle \end{aligned} \quad (8)$$

Wigner - Kirkwood expansion of the Bloch equation for  $U(\beta) = \langle \mathbf{p}_1 \dots \mathbf{p}_N | e^{-\beta H} \mathcal{S} | \mathbf{q}_1 \dots \mathbf{q}_N \rangle$

$$Q_N = \frac{1}{h^{3N} N!} \int d\mathbf{q}_1 \dots d\mathbf{q}_N d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta \left( \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i,j=1}^N V(|\mathbf{q}_i - \mathbf{q}_j|) + \Delta(\mathbf{q}_1, \dots, \mathbf{q}_N) \right)} \quad (9)$$

$$\begin{aligned} \beta \Delta(\mathbf{q}_1, \dots, \mathbf{q}_N) &\rightarrow \left( \frac{\lambda}{r_0} \right)^2 \frac{1}{24\pi} \left[ \sum_{i,j} r_0^2 \nabla_{ij}^2 \beta V(|\mathbf{q}_i - \mathbf{q}_j|) - \left( \sum_{i,j} r_0 \nabla_{ij} \beta V(|\mathbf{q}_i - \mathbf{q}_j|) \right)^2 \right] \\ &\quad - \ln \left( 1 \pm e^{-\pi \left( \frac{r}{\lambda} \right)^2} \right) + \dots \end{aligned} \quad (10)$$

These are the leading order contributions to  $\beta \Delta(\mathbf{q}_1, \dots, \mathbf{q}_N)$  for small  $\lambda/r_0$  where

$$\lambda \equiv \left( \frac{\beta 2\pi \hbar^2}{m} \right)^{1/2}, \quad r_0 = \begin{cases} \text{force range} \\ n^{-1/3} \end{cases}. \quad (11)$$

So the classical limit is expected for "high" temperature and "low" density.

Experimental second virial coefficients (low density gas) for  $\text{H}_2$ ,  $\text{D}_2$ , and  $\text{He}$  indicate domains for validity of  $T > 40^0, 45^0, 75^0 \text{K}$ , respectively. Also accurate for strongly coupled dense equilibrium fluids and solid structure at room temperatures (short ranged potentials).

*What about electrons??* Need  $T \gtrsim 10^5 \text{K}$ . Fully ionized plasma? Still problems.

## II. ELECTRONS AND PROTONS - QUALITATIVE DIFFERENCES BETWEEN QUANTUM AND CLASSICAL

### A. Stability of matter

Classical requirement on the potential in general:

$$\frac{1}{2} \sum_{i,j=1}^N V(|\mathbf{q}_i - \mathbf{q}_j|) \geq -nB, \quad n \geq 0 \quad (12)$$

Not satisfied for system of electrons and protons due to attractive, unbounded Coulomb interaction. Classical matter does not exist!

The corresponding required quantum operator bound is

$$H \geq -nBI, \quad n \geq 0 \quad (13)$$

This is satisfied for a system of electrons and protons (Dyson and Lenard (1968), Lieb (1976)). Quantum matter exists!

## III. EXACT MAPPINGS OF QUANTUM PARTITION FUNCTION TO A CLASSICAL COUNTERPART

### A. Effective many-body potential

$$\begin{aligned} Q_N &= \text{Tr} e^{-\beta H} = \int d\mathbf{q}_1 \dots d\mathbf{q}_N \langle \mathbf{q}_1 \dots \mathbf{q}_N | e^{-\beta H} \mathcal{S} | \mathbf{q}_1 \dots \mathbf{q}_N \rangle \\ &\equiv \frac{1}{N! \lambda^{3N}} \int d\mathbf{q}_1 \dots d\mathbf{q}_N e^{-\beta U(\mathbf{q}_1 \dots \mathbf{q}_N)} \end{aligned} \quad (14)$$

$$\begin{aligned} U_N(\mathbf{q}_1 \dots \mathbf{q}_N) &= -\beta^{-1} \ln N! \lambda^{3N} \langle \mathbf{q}_1 \dots \mathbf{q}_N | e^{-\beta H} \mathcal{S} | \mathbf{q}_1 \dots \mathbf{q}_N \rangle \\ &= U_0 + \frac{1}{2} \sum_{i,j=1}^N V^{(2)}(|\mathbf{q}_i - \mathbf{q}_j|) + \frac{1}{3!} \sum_{i,j,k=1}^N V^{(3)}(|\mathbf{q}_i - \mathbf{q}_j|, |\mathbf{q}_k - \mathbf{q}_j|) + \dots \end{aligned} \quad (15)$$

The classical representation for the quantum partition function in (14) is still exact, including all quantum effects. However, for a Hamiltonian with pairwise additive potentials, the effective potential  $U$  contains many-body potentials of all higher orders. Hence approximations must be used in practice that include only few body potentials.

## B. Quantum particles as classical loops (Sine-Gordon path integral representation)

Expression in terms of microscopic particle densities  $n(\mathbf{r})$ , classical or quantum

$$V \rightarrow \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})V(|\mathbf{r}-\mathbf{r}'|)n(\mathbf{r}'), \quad n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r}-\mathbf{q}_i). \quad (16)$$

In the classical case the partition function is represented in this way in terms of the fields  $n(\mathbf{r})$  instead of the particle configurations.

The classical Sine-Gordon representation is effectively an inverse functional Fourier transform

$$e^{-\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' n(\mathbf{r})V(|\mathbf{r}-\mathbf{r}'|)n(\mathbf{r}')} = \int D[\phi] e^{-\frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \phi(\mathbf{r})V^{-1}(|\mathbf{r}-\mathbf{r}'|)\phi(\mathbf{r}')} e^{-i \int d\mathbf{r} \phi(\mathbf{r})n(\mathbf{r})}, \quad (17)$$

and the Grand Canonical partition function becomes a path integral of the form

$$\Xi(\beta, z) = \sum_N z^N Q_N(\beta) = \int D[\phi] e^{S(\phi)}, \quad (18)$$

where  $S(\phi)$  is the classical action.

The corresponding quantum analysis first starts with the Feynman-Kac representation for  $\langle \mathbf{q}_1 \dots \mathbf{q}_N | e^{-\beta H} \mathcal{S} | \mathbf{q}_1 \dots \mathbf{q}_N \rangle$  followed by the Sine-Gordon representation (Ginibre 1971, Alastuey et al 2008). The first step leads to the introduction of paths, whereby the point particles are replaced by filaments with a Gaussian distribution

$$\mathbf{q}_i \rightarrow \mathbf{q}_i + \lambda \xi_i(s), \quad \langle \xi_i(s) \xi_j(s') \rangle = \delta_{ij} \inf(s, s') (1 - \sup(s, s')) \quad (19)$$

$$V \rightarrow \frac{1}{2} \int_0^1 ds \int d\mathbf{r}d\mathbf{r}' n(\mathbf{r}, s) V(|\mathbf{r}-\mathbf{r}'|) n(\mathbf{r}', s), \quad n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r}-\mathbf{q}_i + \lambda \xi_i(s)). \quad (20)$$

Exchange symmetry implies all paths for the "filaments"  $\xi_i(s)$  are closed. Hence the quantum partition function for particles is the same as the classical form (18).

$$\Xi(\beta, z) = \int D[\phi] e^{S(\phi)}, \quad (21)$$

except that now the classical action describes loops instead of point particles.

#### IV. MOTIVATION FOR SEMI-CLASSICAL REPRESENTATIONS

Why consider semi-classical representation?! Why not just solve the quantum problem? The answer lies in addressing the many-body problem which is common to both classical and quantum representations. Generally, if the state conditions considered do not involve a small parameters (e.g., low density gas, nearly harmonic solid, weakly coupled quasi-particles) the system is strongly correlated and systematic, controlled approximations are rare and limited. However, very effective semi-phenomenological analytic methods have been developed and tested for classical fluids over the past forty years. These include

- resummation of diagrammatic expansions
- integral equations for structure (pair distribution functions)
- perturbation theory about hard core fluids
- finite temperature, non-local density functional theory
- exactly solvable models

In addition, there are simple and accurate numerical methods that are well-developed for classical systems, such as

- Metropolis Monte Carlo simulation
- molecular dynamics simulation and hybrid extensions

Most of these analytic and numerical methods developed for classical systems do not extend directly to the quantum problem, without serious compromises. Molecular dynamics is exceptionally effective for classical systems. For example, for simple atomic systems (e.g., Argon) it describes the gas, liquid, and solid phases as well as their transitions; it also describes transport properties in all phases, and some states far from equilibrium. However, it is based on solving Newton's equations and cannot be simply extended to solve Heisenberg's operator equations.

The exact or approximate mapping of a quantum problem to a corresponding classical representation provides the means to access these classical methods.

## V. TWO PARTICLE QUANTUM POTENTIAL

One of the earliest definitions of a semi-classical potential incorporating quantum effects is based on  $U_N(\mathbf{q}_1.. \mathbf{q}_N)$  in (15) for  $N = 2$ . The idea is to incorporate the diffraction effects of two particles in an effective pair potential that can then be used in classical many-body theory and molecular dynamics simulation. In particular, the short range divergence of attractive Coulomb interactions is removed by such quantum effects, providing a well-defined classical representation of matter (electrons and protons).

Consider a pair of particles of masses  $m_1$  and  $m_2$  and write the Hamiltonian in relative and center of mass variables

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(r), \quad M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{M} \quad (22)$$

For  $N = 2$  (15) becomes, in relative and center of mass coordinate representation

$$U_2(\mathbf{q}_1, \mathbf{q}_2) = -\beta^{-1} \ln \lambda^6 \langle \mathbf{R}, \mathbf{r} | e^{-\beta \left( \frac{P^2}{2M} + \frac{p^2}{2\mu} + V(r) \right)} | \mathbf{R}, \mathbf{r} \rangle. \quad (23)$$

The symmetrization operator  $\mathcal{S}$  does not occur since the particles are different. Since center of mass and relative variables commute, the center of mass contribution can be evaluated simply

$$\langle \mathbf{R} | e^{-\beta \frac{P^2}{2M}} | \mathbf{R} \rangle = \sum_{\mathbf{P}} e^{-\beta \frac{P^2}{2M}} |\langle \mathbf{R} | \mathbf{P} \rangle|^2 = \frac{h^3}{\Omega} \int d\mathbf{P} e^{-\beta \frac{P^2}{2M}} \quad (24)$$

Therefore  $U_2(\mathbf{q}_1, \mathbf{q}_2) = U_2(|\mathbf{q}_1 - \mathbf{q}_2|)$  as expected

$$U_2(r) = -\beta^{-1} \ln \left( \lambda_\mu^3 \langle \mathbf{r} | e^{-\beta \left( \frac{p^2}{2\mu} + V(r) \right)} | \mathbf{r} \rangle \right). \quad (25)$$

where  $\lambda_\mu$  is given by (1) with  $m$  replaced by the reduced mass  $\mu$ .

At this point the calculation of  $U_2(r)$  is reduced to that of a single particle in a central force field. Suppose the eigenvalue problem for the reduced Hamiltonian has been solved

$$\left( \frac{p^2}{2\mu} + V(r) \right) \psi_\alpha = \epsilon_\alpha \psi_\alpha. \quad (26)$$

Then (25) becomes

$$U_2(r) = -\beta^{-1} \ln \left( \lambda_\mu^3 \sum_{\alpha} e^{-\beta \epsilon_\alpha} |\psi_\alpha(\mathbf{r})|^2 \right). \quad (27)$$

This is a numerically tractable problem which has been addressed for special cases, such as the electron - proton Coulomb Hamiltonian (Filinov, 2004). However, for practical purposes and applications it is useful to have simpler forms from approximations. Two of these are now discussed.

### A. Weak coupling approximation

Consider the special case of the Coulomb interaction  $V(r) = q_1 q_2 / r$ . A dimensionless coupling constant is defined in terms of the Coulomb energy for a pair at their average distance  $r_0$  relative to the kinetic energy

$$\Gamma = \frac{\beta q_1 q_2}{r_0}. \quad (28)$$

Typically  $r_0 \sim n^{-1/3}$ . For conditions such that  $\Gamma \ll 1$  the right side of (25) can be expanded to first order in  $V$ . This is accomplished using the identity

$$e^{-\beta\left(\frac{p^2}{2\mu} + V(r)\right)} = e^{-\beta\frac{p^2}{2\mu}} - \int_0^\beta d\beta' e^{(\beta' - \beta)\frac{p^2}{2\mu}} V(r) e^{-\beta'\frac{p^2}{2\mu}} + \dots \quad (29)$$

where the dots denote contributions of higher degree in  $V$ . Substitution into (25) and expanding the log to leading order in  $V$  gives

$$U_2(r) = \beta^{-1} \lambda_\mu^3 \int_0^\beta d\beta' \langle \mathbf{r} | e^{(\beta' - \beta)\frac{p^2}{2\mu}} V(r) e^{-\beta'\frac{p^2}{2\mu}} | \mathbf{r} \rangle + \dots \quad (30)$$

This expression can be evaluated exactly with the result

$$U_2(r) \equiv \int d\mathbf{r}' \Pi(r') V(\mathbf{r} - \mathbf{r}'), \quad \Pi(r) = 2 \frac{\lambda_\mu}{r} e^{-4\pi(r/\lambda_\mu)^2}. \quad (31)$$

Equation (31) shows that the quantum effects are a smoothing of the original potential over region of the size of the thermal wavelength  $\lambda_\mu$ . Equation (30) shows that the origin of these effects is the non-commutation of kinetic and potential energies. Finally, performing the integral in (31) gives

$$U_2(r) = \frac{q_1 q_2}{r} S(r), \quad (32)$$

where the quantum regularization  $S(r)$  is

$$S(r) = 1 - e^{-4\pi(r/\lambda_\mu)^2} - 2\pi \frac{r}{\lambda_\mu} (\operatorname{erf}(2\sqrt{\pi}r/\lambda_\mu) - 1) \quad (33)$$

The functional forms for  $S(r)$  and  $U_2(r)$  as functions of  $r/\lambda_\mu$  are shown in Figure 1. The important observations are that the modifications due to  $S(r)$  cross over to unity for  $r/\lambda_\mu \gg 1$ , indicating that the Coulomb form applies on large scales. Also  $S(r)$  becomes proportional to  $r$  at short distances so the Coulomb singularity is removed.



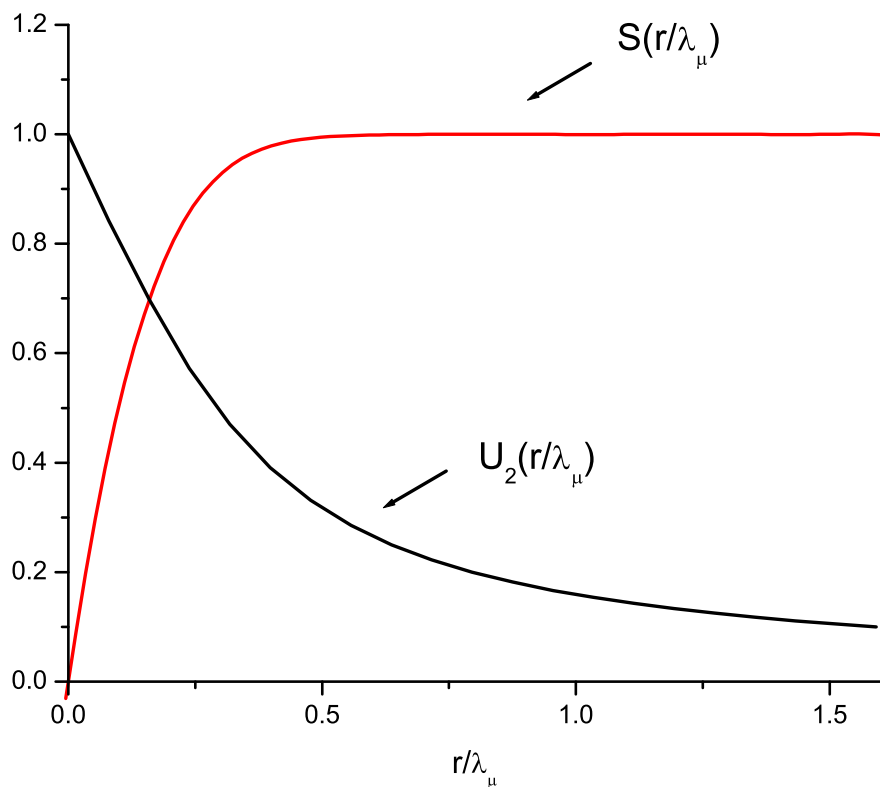


FIG. 1: Dependence of  $S(r)$  and  $U_2(r)$  on  $r/\lambda_\mu$ .

### B. Degeneracy effects

To describe the effects of degeneracy, consider  $N$  identical particles (Bosons or Fermions) of mass  $m$  interacting with a single impurity of mass  $m_0$  via a central potential  $V(r)$ . The Hamiltonian is

$$H = \frac{p_0^2}{2m_0} + \sum_{\alpha=1}^N \left( \frac{p_\alpha^2}{2m} + V(|\mathbf{q}_\alpha - \mathbf{q}_0|) \right) \quad (34)$$

The effective interaction of any electron with the impurity will be affected by exchange symmetry with the remaining electrons. To simplify the discussion, assume the impurity has infinite mass and is located at the origin. In this case the effective classical potential is defined by

$$\langle r | \left( e^{\beta \left( \frac{p^2}{2m} + \hat{V} - \mu \right)} + 1 \right)^{-1} | r \rangle \equiv (2\pi\hbar)^{-3} \int d\mathbf{p} \left( e^{\beta \left( \frac{p^2}{2m} - \mu + U(r) \right)} + 1 \right)^{-1}. \quad (35)$$

The left side is the exact quantum representation for the average density  $n(r)$  of electrons about the impurity, while the right side defines a semi-classical form as a function of the quantum potential  $U(r)$ . The integrand of the right side is an ordinary function while the left side involves corresponding operators. This particular definition is chosen such that  $U(r)$  vanishes when  $\widehat{V}(r)$  vanishes.

A weak coupling expansion of  $U(r)$  to linear order in  $\widehat{V}(r)$  can be performed just as above leading to the form (31) except that the smoothing function  $\Pi(r')$  is more complex, including the degeneracy effects. The resulting expression for  $U(r)$  is found to be

$$U(r) = \frac{q_1 q_2}{r} S(r), \quad (36)$$

$$S(r) \rightarrow \frac{8r}{\lambda} \frac{\partial \ln z}{\partial (n\lambda^3)} \int_0^\infty dx x \frac{1}{z^{-1}e^{x^2} + 1} \left( \frac{\lambda}{4\sqrt{\pi}xr} (1 - \cos(x4\sqrt{\pi}r/\lambda)) + \left( \frac{1}{2}\pi - \text{Si}(x4\sqrt{\pi}r/\lambda) \right) \right). \quad (37)$$

It is easily verified that (33) is recovered in the non-degenerate limit ( $z \ll 1$ ). In the opposite limit of very strong degeneracy the quantum modifications of  $S(r)$  are shown in Figure 2. As in the non-degenerate case  $S(r)$  is linear at small  $r$  showing that the classical Coulomb divergence is removed. It crosses over to unity at large  $r$ , recovering the Coulomb form at large scales. However, there are now oscillations in the crossover domain (Friedel oscillations).

### C. Variational approximation (Feynman-Kleinert)

Consider again the two particle partition function without degeneracy. A nonperturbative approximation for  $U_2(r)$  was introduced by Feynman and Kleinert (1986). The basic idea is to use a variational principle. They reformulate the above in terms of the two particle partition function in the Feynman-Kac path integral representation

$$Q_2 = \int d\mathbf{r} \langle \mathbf{r} | e^{-\beta \left( \frac{p^2}{2\mu} + V(r) \right)} | \mathbf{r} \rangle = \int D[x(\tau)] \exp \left\{ -\frac{1}{\hbar} \mathcal{A}[x(\tau)] \right\} \quad (38)$$

where the action  $\mathcal{A}[x(\tau)]$  is

$$\mathcal{A}[x(\tau)] = \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \left[ \frac{\mu}{2} \dot{x}^2(\tau) + V(x(\tau)) \right] \quad (39)$$

The paths  $x(\tau)$  can be written as their average values plus the deviation from these averages

$$x(\tau) = x_0 + \delta x(\tau), \quad x_0 = \frac{1}{\hbar\beta} \int_0^{\hbar\beta} d\tau x(\tau), \quad (40)$$

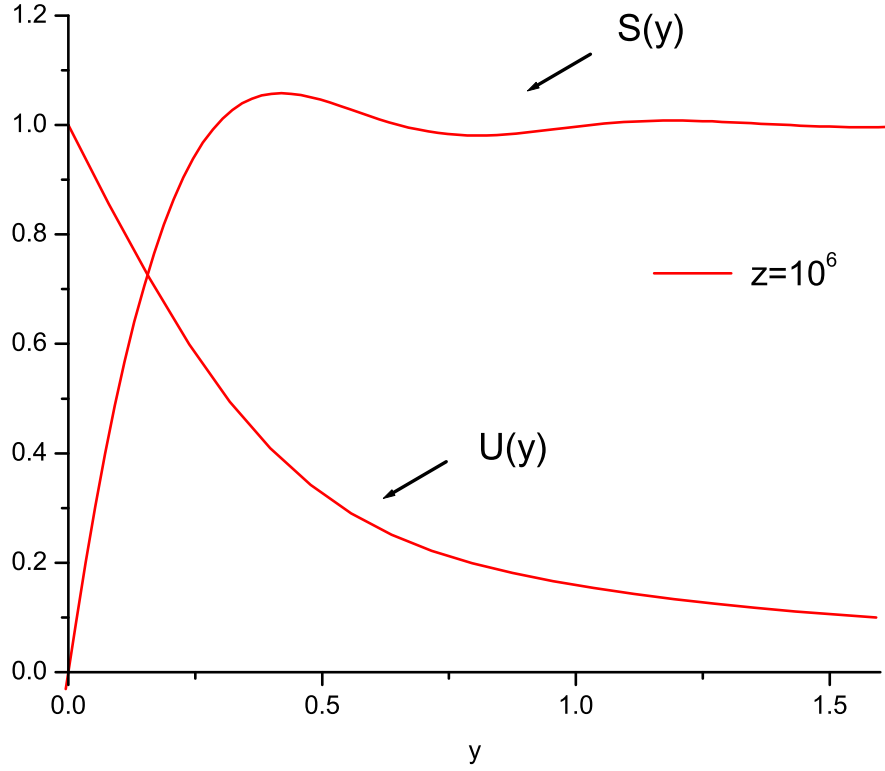


FIG. 2: Dependence of  $S(r)$  and  $U(r)$  on scaled distance for  $z = 10^6$ .

so that (38) can be written as an ordinary integral over  $x_0$  and a functional integral over the deviation paths

$$Q_2 = \int d\mathbf{x}_0 \int D[x(\tau)] \exp \left\{ -\frac{1}{\hbar} \mathcal{A}[x_0 + \delta x(\tau)] \right\} = \lambda_\mu^{-3} \int d\mathbf{r} e^{-\beta U_2(r)}$$

Rewrite this by dividing  $\mathcal{A}[x(\tau)]$  into a simple reference part  $\mathcal{A}_0[x(\tau)]$  and its remainder  $\mathcal{A}_1[x(\tau)]$

$$\begin{aligned} Q_2 &= \int D[x(\tau)] \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_0[x(\tau)] \right\} \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_1[x(\tau)] \right\} \\ &= Q_2^{(0)} \left\langle \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_1[x(\tau)] \right\} \right\rangle^{(0)}, \end{aligned} \quad (41)$$

Where  $\langle X \rangle^{(0)}$  means

$$\langle X \rangle^{(0)} = \frac{1}{Q_2^{(0)}} \int D[x(\tau)] \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_0[x(\tau)] \right\} X \quad (42)$$

$$Q_2^{(0)} = \int D[x(\tau)] \exp \left\{ -\frac{1}{\hbar} \mathcal{A}_0 [x(\tau)] \right\} \quad (43)$$

From the convexity of  $e^x$  it follows that

$$Q_2 \geq Q_2^{(0)} \exp \left\{ -\frac{1}{\hbar} \langle \mathcal{A}_1 [x(\tau)] \rangle^{(0)} \right\}, \quad (44)$$

Then, by an appropriate parameterized choice for  $\mathcal{A}_0 [x_0 + \delta x(\tau)]$  such that the calculations for the reference action can be done exactly, the right side of (44) can be optimized to give a good approximation for  $U_2(r)$ . For the details, refer to the original paper of Feynman and Kleinert (1986).

#### D. Phenomenological optimization of the weak coupling form

Consider again the weak coupling approximation for  $U_2(r)$  given by (32) and (33)

$$\begin{aligned} U_2(r) &= -\beta^{-1} \ln \left( \lambda_\mu^3 \sum_\alpha e^{-\beta \epsilon_\alpha} |\psi_\alpha(\mathbf{r})|^2 \right) \\ &\rightarrow \frac{q_1 q_2}{r} \left[ 1 - e^{-4\pi(r/\lambda_\mu)^2} - 2\pi \frac{r}{\lambda_\mu} (\operatorname{erf}(2\sqrt{\pi}r/\lambda_\mu) - 1) \right] \end{aligned} \quad (45)$$

The exact value of  $U_2(0) = -\beta^{-1} \ln (\lambda_\mu^3 \sum_\alpha e^{-\beta \epsilon_\alpha} |\psi_\alpha(\mathbf{0})|^2)$  is known, and can be incorporated by parameterizing the weak coupling form to give an improved result

$$U_2(r) \rightarrow \frac{q_1 q_2}{r} \left[ 1 - e^{-4\pi(r/\lambda_\mu)^2} - 2\pi \gamma \frac{r}{\lambda_\mu} (\operatorname{erf}(2\sqrt{\pi}r/\gamma\lambda_\mu) - 1) \right], \quad (46)$$

with

$$\gamma = \frac{2\pi q_1 q_2}{\lambda_\mu U_2(0)}. \quad (47)$$

This inclusion of the exact (all orders in  $V$ ) property  $U_2(0)$  in the functional form (45) improves the quantitative prediction over all values for  $r$  significantly. Applications of this potential to Hydrogen using molecular dynamics will be illustrated in later lectures by Bonitz.

## VI. WAVE PACKET MOLECULAR DYNAMICS

All of the above relationship between classical and quantum descriptions has been based on equilibrium properties, mainly the partition function and its representations. The resulting potentials of the last section are characterized by quantum effects measured through

the thermal wavelength  $\lambda$ . However, in many cases it is of interest to use classical methods for nonequilibrium properties and associated quantum potentials not prejudiced to the equilibrium state are desired. One approach to this problem is provided by the method of wavepacket molecular dynamics.

To simplify the discussion consider a single electron in the presence of a fixed ion with charge number  $Z$ . The expectation value of an operator depending only on the position and momentum coordinates can be expressed in terms of its Weyl representation

$$\begin{aligned}\langle A(\hat{\mathbf{r}}, \hat{\mathbf{p}}) \rangle &= (2\pi)^{-6} \int d\lambda d\eta \tilde{A}_{cl}(\lambda, \eta) \langle e^{i(\lambda \cdot \hat{\mathbf{r}} + \eta \cdot \hat{\mathbf{p}})} \rangle \\ &= \int d\mathbf{r} d\mathbf{p} A_{cl}(\mathbf{r}, \mathbf{p}) (2\pi)^{-6} \int d\lambda d\eta A \langle e^{i(\lambda \cdot (\hat{\mathbf{r}} - \mathbf{r}) + \eta \cdot (\hat{\mathbf{p}} - \mathbf{p}))} \rangle \\ &= \int d\mathbf{r} d\mathbf{p} A_{cl}(\mathbf{r}, \mathbf{p}) P(\mathbf{r}, \mathbf{p}).\end{aligned}\quad (48)$$

Here  $A_{cl}(\mathbf{r}, \mathbf{p})$  is the classical phase function associated with the operator  $A(\hat{\mathbf{r}}, \hat{\mathbf{p}})$  and  $\tilde{A}_{cl}(\lambda, \eta)$  is its Fourier transform. The last line of (48) expresses the expectation value as a classical average over the "probability density  $P(\mathbf{r}, \mathbf{p})$ "

$$\begin{aligned}P(\mathbf{r}, \mathbf{p}) &= (2\pi)^{-6} \int d\lambda d\eta \langle e^{i(\lambda \cdot (\hat{\mathbf{r}} - \mathbf{r}) + \eta \cdot (\hat{\mathbf{p}} - \mathbf{p}))} \rangle \\ &= (2\pi)^{-6} \int d\lambda d\eta e^{\frac{i}{2}\hbar\lambda \cdot \eta} \langle e^{i\lambda \cdot (\hat{\mathbf{r}} - \mathbf{r})} e^{i\eta \cdot (\hat{\mathbf{p}} - \mathbf{p})} \rangle.\end{aligned}\quad (49)$$

This is not a complete correspondence between classical and quantum descriptions, since it can be shown that  $P(\mathbf{r}, \mathbf{p})$  is not positive definite. In later lectures, this will be related to the Wigner function representation of quantum mechanics.

For a pure state  $\psi(\mathbf{r})$

$$P(\mathbf{r}, \mathbf{p}) = (2\pi)^{-6} \int d\lambda d\eta e^{\frac{i}{2}\hbar\lambda \cdot \eta} \int d\mathbf{r}' \psi^*(\mathbf{r}') e^{i\lambda \cdot (\hat{\mathbf{r}} - \mathbf{r})} e^{i\eta \cdot (\hat{\mathbf{p}} - \mathbf{p})} \psi(\mathbf{r}'). \quad (50)$$

A special case is given by the Gaussian wavepacket  $\psi(\mathbf{r} | x)$

$$\psi(\mathbf{r} | x) = \left(\frac{2a}{\pi}\right)^{3/4} \exp\left[-\left(a + \frac{i}{\hbar}b\right)(\mathbf{r} - \mathbf{r}_0)^2 - \frac{i}{\hbar}\mathbf{p}_0 \cdot (\mathbf{r} - \mathbf{r}_0)\right] \quad (51)$$

where  $x$  denotes the set of parameters  $\{a, b, \mathbf{r}_0, \mathbf{p}_0\}$ . It is easily verified that the parameters  $\mathbf{r}_0$  and  $\mathbf{p}_0$  are the expectation values for the position and momentum of the electron, respectively. The additional parameters characterized the width and its rate of change. A more general mixed state is given by

$$P(\mathbf{r}, \mathbf{p}) = (2\pi)^{-6} \int d\lambda d\eta e^{\frac{i}{2}\hbar\lambda \cdot \eta} \text{Tr} \rho e^{i\lambda \cdot (\hat{\mathbf{r}} - \mathbf{r})} e^{i\eta \cdot (\hat{\mathbf{p}} - \mathbf{p})}, \quad (52)$$

where  $\rho$  is the density matrix

$$\rho = \int dx f(x) P_{\psi(\mathbf{r}|x)}, \quad (53)$$

and  $P_{\psi(\mathbf{r}|x)}$  is the projection onto  $\psi(\mathbf{r} | x)$ .

As a practical approximation assume that the form of  $\psi(\mathbf{r} | x)$  in (51) is preserved in time

$$\psi(\mathbf{r} | x) \rightarrow \psi(\mathbf{r} | x(t)), \quad (54)$$

where the time dependence of the parameters  $x(t)$  is determined from the variational principle

$$\delta \langle (i\hbar\partial_t - H) \rangle_{\psi(\mathbf{r}|x)} = 0. \quad (55)$$

The resulting set of equations are similar to classical Hamilton's equations

$$\begin{aligned} \dot{\mathbf{r}}_0 &= \nabla_{\mathbf{p}_0} H_{eff}, & \dot{\mathbf{p}}_0 &= -\nabla_{\mathbf{r}_0} H_{eff}, & \dot{a} &= \nabla_b H_{eff}, & \dot{b} &= -\nabla_a H_{eff} \\ H_{eff} &= \frac{p_0^2}{2m} + \frac{3a^2}{2m} (b^2 + 1) + V_{eff}, & V_{eff} &= -\frac{Ze^2}{r_0} \text{erf}(r_0/a) \end{aligned}$$

The differences here are an effective ion-electron potential that removes the Coulomb singularity within a distance of  $a$ , and an expanded phase space to include the width of the packet  $a$  and its conjugate momentum  $b$ ,

Further details of these approach and a recent application to Hydrogen can be found in Jacob et al (2007).

## VII. ORBITAL FREE DENSITY FUNCTIONAL THEORY

A final application of semi-classical representations for quantum systems occurs in "orbital free" density functional theory. Consider a quantum system in the presence of external sources that can be described by an additive potential

$$\hat{V} = \sum_{i=1}^N V(\mathbf{q}_i) = \int d\mathbf{r} V(\mathbf{r}) \hat{n}(\mathbf{r}), \quad (56)$$

where  $\hat{n}(\mathbf{r})$  is the number density operator as in (16). The details of the remainder of the Hamiltonian are not important at this point. The theorems of density functional theory apply in the following form. First, a functional of the average density  $n_e(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle$ ,

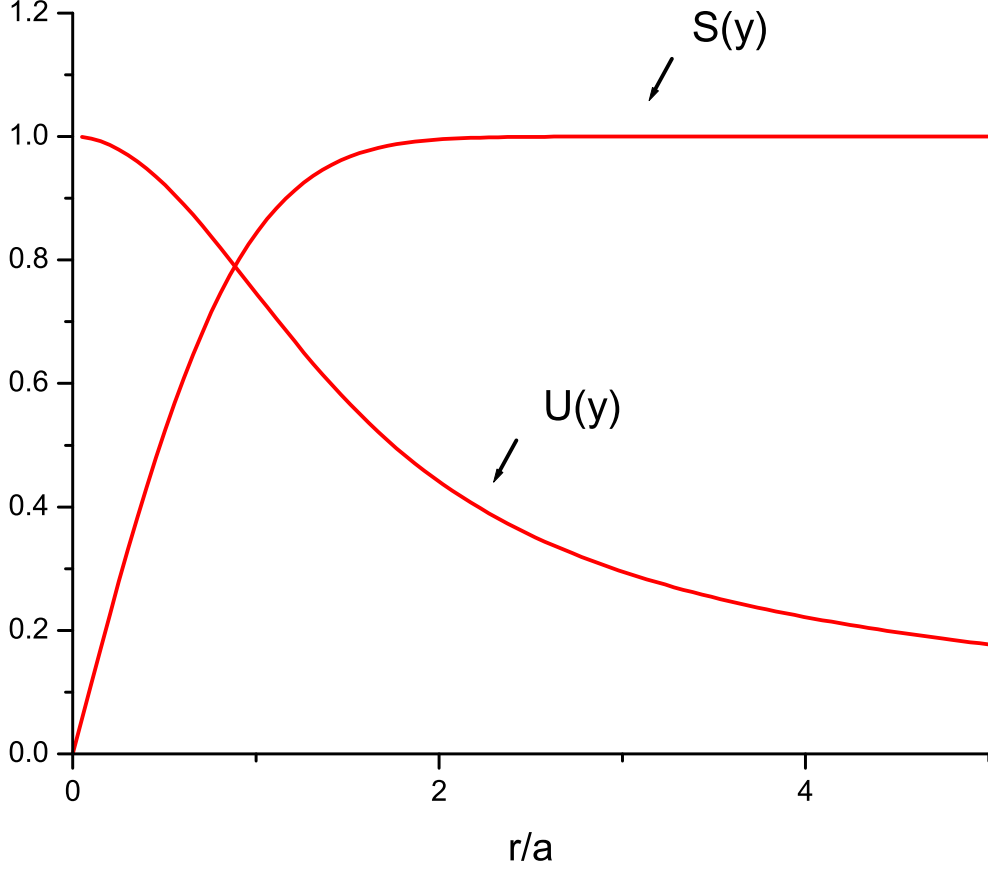


FIG. 3: Dependence of  $S(r) = \text{erf}(r)$  and  $U(r)$  on  $r/a$

averaged over an equilibrium grand canonical ensemble, is constructed in two steps. First, the equilibrium grand potential for the system is considered formally

$$\beta\Omega_e = -\ln \text{Tr} e^{-\beta(H-\mu N)}. \quad (57)$$

The density is obtained (formally) by functional differentiation with respect to the potential

$$\Omega_e = \Omega_e(\mu - V), \quad n_e(r) = -\frac{\delta\Omega_e}{\delta[\mu - V(r)]}. \quad (58)$$

The density equation is inverted (formally) to get the external potentials as a functional of the average density

$$V_\alpha = \mathcal{V}_\alpha(\mathbf{r} | n_e), \quad (59)$$

and a Legendre transformation is performed to construct the free energy as a functional of the densities rather than the chemical potentials

$$F(n_{e\alpha}) = \Omega_e(\mu - \mathcal{V}) + \int d\mathbf{r} [\mu - \mathcal{V}(\mathbf{r} | n_e)] n_e(\mathbf{r}). \quad (60)$$

The crucial second step is to extend this functional to *arbitrary density fields*

$$F(\{n_e\}) \rightarrow F(\{n\}). \quad (61)$$

The main task of density functional theory is now to construct the density functional

$$\Omega_V(n) \equiv F(n) - \int d\mathbf{r} (\mu - V(\mathbf{r})) n(\mathbf{r}), \quad (62)$$

where, in this definition,  $V(\mathbf{r})$  is *not* considered to be a functional of the density. The main theorem of density functional theory is then that this functional has an extremum at the equilibrium density

$$\frac{\delta\Omega_V(n)}{\delta n} = 0 = \frac{\delta F(n)}{\delta n} - [\mu - V(\mathbf{r})], \quad \Rightarrow n = n_e. \quad (63)$$

Furthermore the value of the functional at the equilibrium density is clearly the equilibrium grand potential  $\Omega_V(n) = \Omega(\mu - \mathcal{V})$ . In practice, an approximate free energy functional  $F(\{n\})$  is written and Eq. (63) is solved to obtain the equilibrium density. This density is then used to evaluate the equilibrium grand potential and determine all equilibrium thermodynamic properties.

How should the functional  $F(n)$  be constructed? There is clearly a part associated with an ideal gas, and an energy due to the direct Coulomb interactions. In addition there are the more difficult parts due to exchange and correlations. Consequently, it has become standard practice to write the free energy as

$$F[n] = F^{(0)}(n) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' V_c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') + F_{xc}(n), \quad (64)$$

where  $F^{(0)}(n)$  is the free energy for the non-interacting system, the second term is the contribution from the direct Coulomb interaction, and  $F_{xc}(n)$  denotes the remaining contributions due to interactions from exchange and correlations. Then the extremum condition (9) becomes

$$\mathcal{V}^{(0)}(\mathbf{r} | n) = V(\mathbf{r}) + \int d\mathbf{r} d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') + \frac{\delta F_{xc}(n)}{\delta n_\alpha(\mathbf{r})}, \quad (65)$$

with  $\mathcal{V}^{(0)}(\mathbf{r} | n)$  denoting the functional (59) for the non-interacting system. Determination of this functional is the central issue of the discussion here, and is closely related to the quantum potentials above.

Traditionally, (65) is converted into an equivalent Kohn-Sham self-consistent effective single particle Schroedinger equations which are solved for the orbitals  $\psi_i(r)$ , and the density



is constructed from them and the associated eigenvalues according to

$$n(r) = \langle r | \left( e^{\beta \left( \frac{p^2}{2m} + \hat{V} - \mu \right)} + 1 \right)^{-1} | r \rangle = \sum_i (e^{\beta(\epsilon_i - \mu)} + 1)^{-1} |\psi_i(r)|^2. \quad (66)$$

This avoids the difficult problem of finding the functional  $\mathcal{V}_\alpha^{(0)}(\mathbf{r} | n)$  but at the cost of having to solve a set of self-consistent Schrodinger equations. An alternative approach ("orbital free") attempts to construct the functional  $\mathcal{V}^{(0)}(\mathbf{r} | n)$  directly. The definition of the functional  $\mathcal{V}^{(0)}(\mathbf{r} | n)$  is straightforward from the representation of the density for the non-interacting system in the external potentials

$$n(r) = \langle r | \left( e^{\beta \left( \frac{p^2}{2m} + \hat{V} - \mu \right)} + 1 \right)^{-1} | r \rangle \quad (67)$$

which is just the left side of (35). This must be inverted to find  $\mathcal{V}^{(0)}(\mathbf{r} | n)$ .

The inversion can be done in two steps, in terms of the quantum potential defined by (35). First the latter is solved to give  $U(r)$  as a functional of  $V(r)$ . Then (35) defines the functional relationship of  $U(r | V)$  to  $n(r)$

$$n(r) \equiv \int \frac{d\mathbf{p}}{(2\pi\hbar)^3} \left( e^{\beta \left( \frac{p^2}{2m} + U(r|V) - \mu \right)} + 1 \right)^{-1}. \quad (68)$$

This is just the well-known ideal gas relationship of the chemical potential to the density. Thus, the determination of  $\mathcal{V}^{(0)}(\mathbf{r} | n)$  is seen to be effectively the same as that of determining the quantum potential  $U(r | V)$ . Once this is accomplished, (65) becomes a classical nonlinear integral equation for the density, without the need to solve the Kohn-Sham equations.

It is instructive to consider the non-degenerate limit. In that case the polarization function is evaluated using  $F_0(p) \rightarrow e^{-\beta \left( \frac{p^2}{2m} - \mu \right)}$ . Furthermore, Eq. (68) simplifies to

$$n(r) = n e^{-\beta U(r)}, \quad (69)$$

and the weak coupling quantum potential is

$$U(r') = \int d\mathbf{r}' \pi(r') \mathcal{V}^{(0)}(\mathbf{r} - \mathbf{r}'). \quad (70)$$

Use of these in the DFT equation (65) gives the closed equation for the densities

$$\ln \frac{n(r)}{n} = -\beta \bar{V}(\mathbf{r}) - \beta \int d\mathbf{r} d\mathbf{r}' \bar{V}_c(\mathbf{r} - \mathbf{r}') n(\mathbf{r}') + \int d\mathbf{r}' \pi(\mathbf{r} - \mathbf{r}') \frac{\delta F_{xc}(\{n\})}{\delta n(\mathbf{r}')}. \quad (71)$$

The potentials  $\bar{V}(\mathbf{r})$  and  $\bar{V}_c(\mathbf{r} - \mathbf{r}')$  are “regularized” by the polarization function, e.g.,

$$\bar{V}(\mathbf{r}) = \int d\mathbf{r}' \pi(r') V(\mathbf{r} - \mathbf{r}'). \quad (72)$$

In the weak coupling limit where  $F_{xc}(\{n\})$  can be neglected (65) becomes the usual Boltzmann-Poisson equation with effective quantum potentials given by (33).