Plan of the lectures

1. Introductory remarks on metallic nanostructures
   - Relevant quantities and typical physical parameters
   - Applications
2. Linear electron response: Mie theory and generalizations
3. **Nonlinear response (mean field)**
   - **Survey of various models from N-body to macroscopic**
   - **Mean-field approximation (Hartree and Vlasov equations)**
4. Beyond the mean-field approximation
   - Hartree-Fock equations
   - Time-dependent density functional theory (DFT) and local-density approximation (LDA)
5. Macroscopic models: quantum hydrodynamics

   Linear theory and comparison of various models
6. Spin dynamics: experimental results and recent theoretical advances
7. Illustration: the nonlinear electron dynamics in thin metal films

Mie theory of the surface plasmon – overview

Hypotheses

- Linear response
- Classical

Results

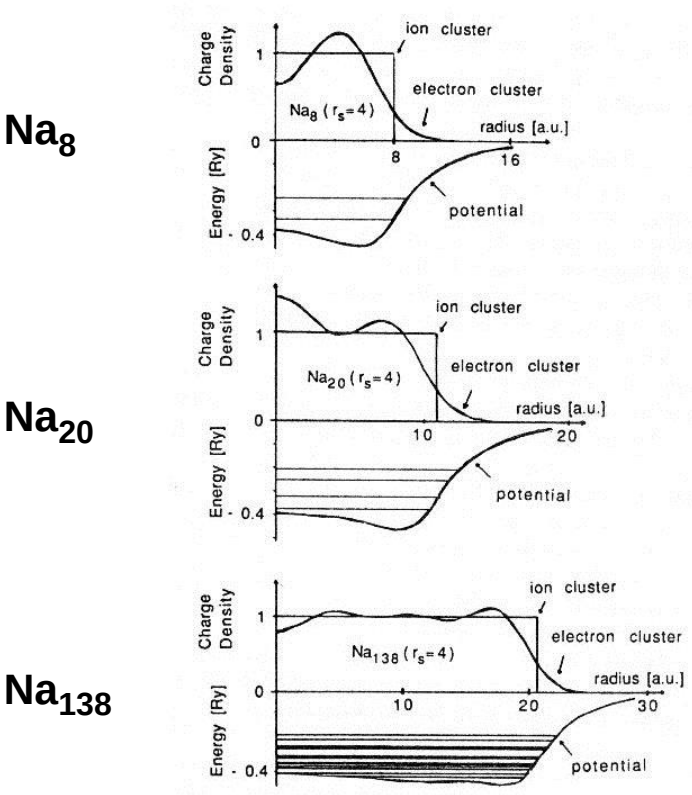
- Frequency: $\omega \approx \omega_{\mathrm{Mie}}\left(1 - K\, N^{-1/3}\right)$
- Linewidth: $\Gamma = \Gamma_{\infty} + A\dfrac{V_F}{R} \propto N^{-1/3}$

Beyond Mie Theory

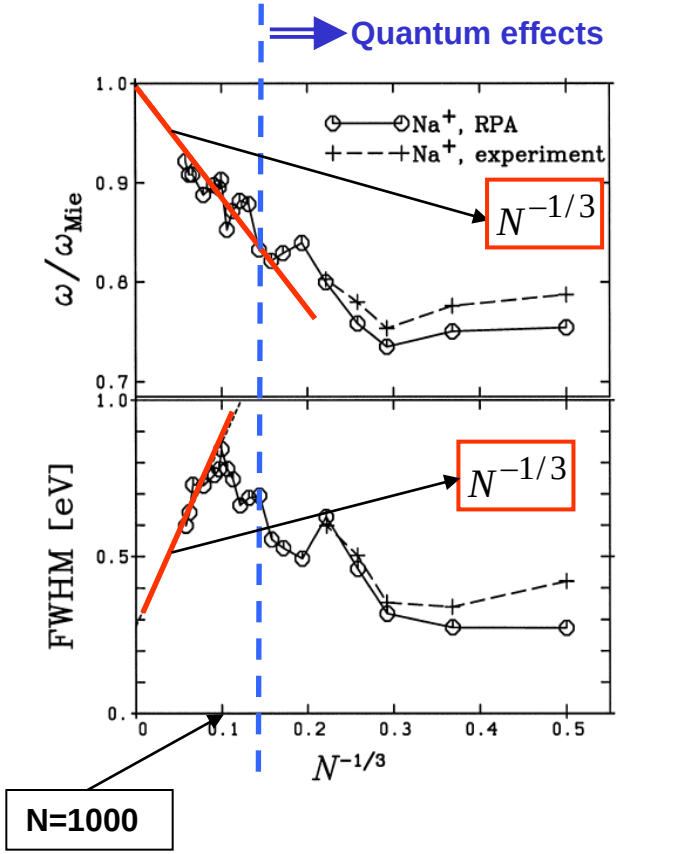
- **Quantum effects** ($\lambda_B \sim R$)
  - Discrete energy levels
- **Nonlinear effects**
  - Large excitations

Quantum effects – examples

- Discrete energy levels
- Ground state spatial oscillations
- Quantum effects are more prominent for small nanoparticles



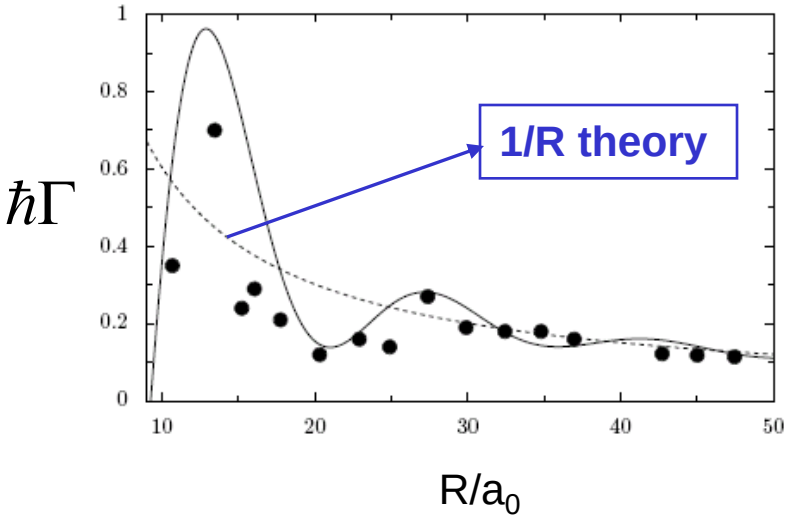
U. Kreibig and M. Vollmer, Optical properties of metal clusters, (Springer 1995).



F. Calvayrac et al., Phys. Rep. **337**, 493-578 (2000).

Quantum effects – examples

Quantum oscillations in the damping rate



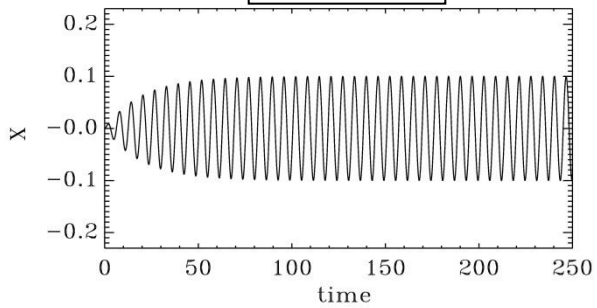
G. Weick, PhD thesis, IPCMS, Strasbourg (2006)

Nonlinear effects – the forced nonlinear oscillator

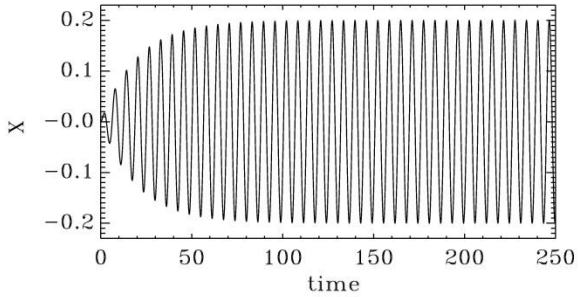
$$\frac{d^2x}{dt^2} + \omega_0{}^2 x + \Gamma \frac{dx}{dt} + Kx^3 = F_0 \cos(\omega\, t)$$

Linear force | Friction | Nonlinearity | Forcing

$F_0 = 0.01$



$F_0 = 0.02$



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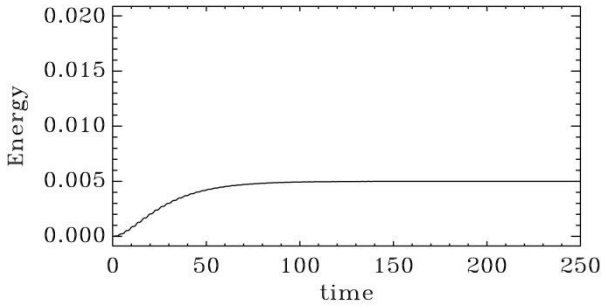
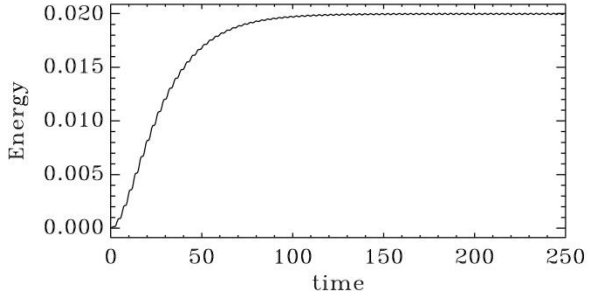
Linear regime: response proportional to excitation





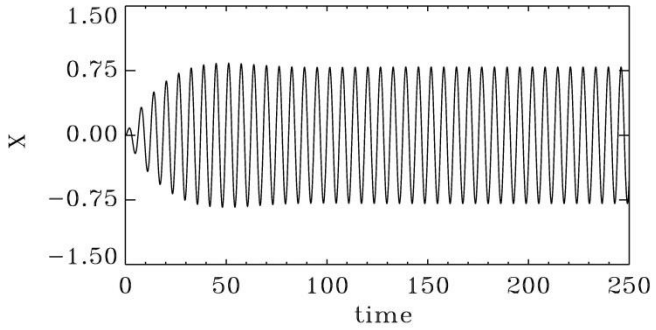
X 4

Nonlinear effects – the forced nonlinear oscillator

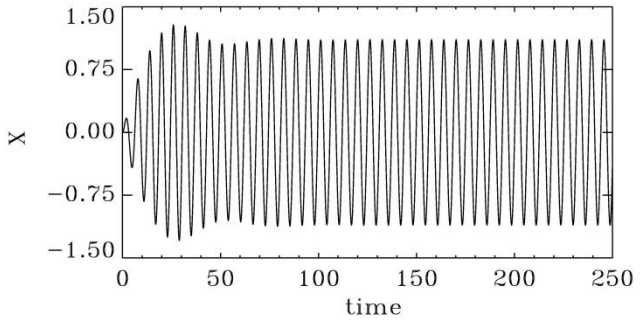
$$\frac{d^2x}{dt^2} + \omega_0^2 x + \Gamma \frac{dx}{dt} + Kx^3 = F_0 \cos(\omega t)$$

Linear force | Friction | Nonlinearity | Forcing

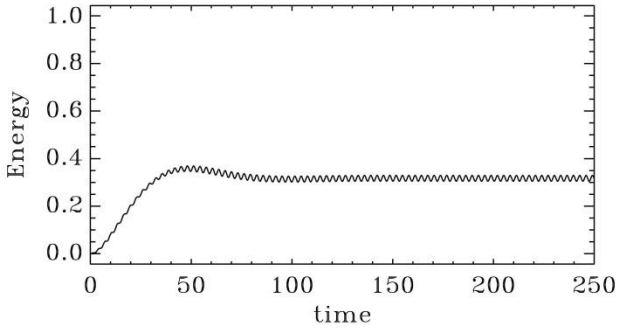
$F_0 = 0.1$

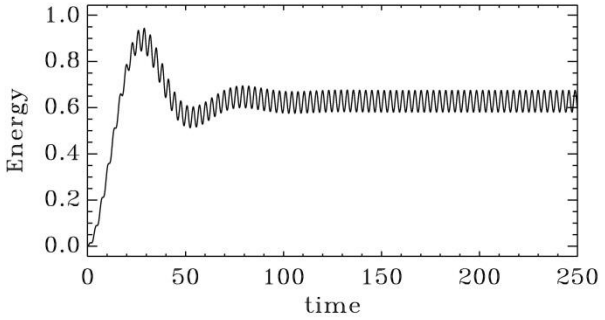


$F_0 = 0.2$



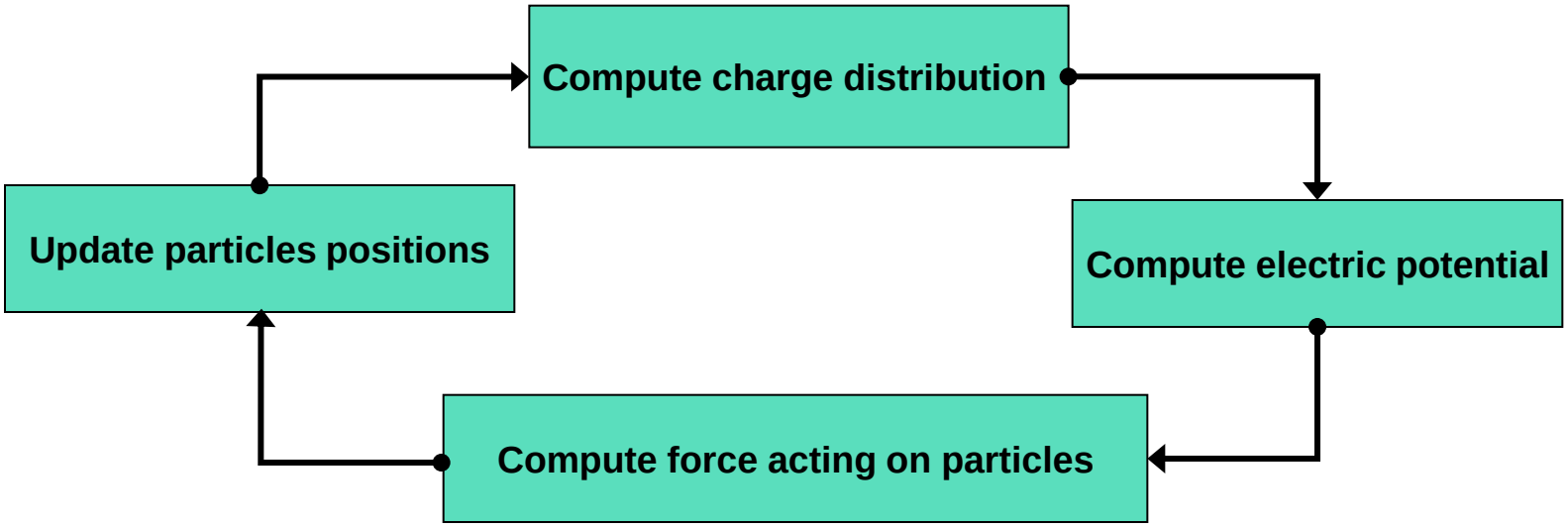
Noninear regime: response NOT proportional to excitation





Nonlinear effects in an electron gas

- The particle motion modifies the internal electric fields…
- … which, in turn, affects the electron dynamics …
- … and so on …



"Self-consistency"

Quantum many-body dynamics

- The most general quantum-mechanical model relies on the N-body wave function: $\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N, t)$
- N-body Hamiltonian

$$H = \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2 + \sum_{i>j}^{N} \frac{e^2}{4\pi\epsilon|\boldsymbol{r}_i - \boldsymbol{r}_j|} + \sum_{i=1}^{N} V_{ext}(\boldsymbol{r}_i)$$

e-e interactions

$V_{ext} = V_{ion}(r) + V_{laser}(r,t)$

- This is VERY hard to solve.
- Example: 3 particles
  - Configuration space (r_1, r_2, r_3) is 9-dimensional
  - Mesh with 100 points per axis → 10^{18} points!
- We look for a <u>one-body</u> formulation of the many-body problem
  - Considerable simplification for numerical solution
- As a first approximation, we can write: $\psi = \psi_1(r_1) \times \psi_2(r_2) \times \ldots \times \psi_N(r_N)$

Derivation of the stationary Hartree equations (1927)

- A solution of the Schrödinger eq. is given by a state that minimizes: $\langle \Psi | H | \Psi \rangle$
- Assume wave function can be factored into the product of N one-body wave functions

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, t) = \psi_1(\boldsymbol{r}_1, t)\ \psi_2(\boldsymbol{r}_2, t) \ldots \psi_N(\boldsymbol{r}_N, t)$$

- Compute expectation value of the energy:

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{N} \int d\mathrm{r}\ \psi_i^*(\mathrm{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V_{ext}(\mathrm{r}) \right) \psi_i(\mathrm{r}) + \frac{e^2}{4\pi\epsilon} \sum_{i>j}^{N} \int\int d\mathrm{r}\, d\mathrm{r}' \frac{|\psi_i(\mathrm{r})|^2 |\psi_j(\mathrm{r}')|^2}{|\mathrm{r}_i - \mathrm{r}_j|}$$

- Minimize keeping total number of particles fixed

$$\frac{\delta}{\delta \psi_i^*} \left\{ \langle \Psi | H | \Psi \rangle - \sum_i \varepsilon_i \int d\mathrm{r}\ |\psi_i(\mathrm{r})|^2 \right\} = 0$$

- Obtain **Hartree equations**

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_k(\mathrm{r}) + V_{ext}(\mathrm{r}) \psi_k(\mathrm{r}) + \frac{e^2}{4\pi\epsilon} \sum_{j=1}^{N} \int d\mathrm{r}' \frac{|\psi_j(\mathrm{r}')|^2}{|\mathrm{r} - \mathrm{r}'|} \psi_k(\mathrm{r}) = \varepsilon_k \psi_k(\mathrm{r}) \qquad k=1 \ldots N$$

"Hartree potential"

$-eV_H$

Stationary Hartree equations

"Hartree potential"

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(\mathrm{r}) + V_{ext}(\mathrm{r})\psi_k(\mathrm{r}) - eV_H(\mathrm{r})\psi_k(\mathrm{r}) = \varepsilon_k\psi_k(\mathrm{r}) \qquad k=1...N$$

$$\Delta V_H = \frac{e}{\varepsilon}\sum_{j=1}^{N} p_j|\psi_j(\mathrm{r})|^2$$

Poisson's equation

Electronic density

$$n(\mathrm{r}) \equiv \sum_{j=1}^{N} p_j|\psi_j(\mathrm{r})|^2$$

Occupation numbers: $\boldsymbol{p_j}$

Allow to define Fermi-Dirac distribution at finite temperature:

$$p_j = [1 + \exp\{(\varepsilon_j - \mu)/k_B T_e\}]^{-1}$$

Time-dependent Hartree equations

- Formally replace $H\psi_k = \varepsilon_k \psi_k$ with $H\psi_k = i\hbar \dfrac{\partial \psi_k}{\partial t}$

- Obtain time-dependent Hartree equations

$$i\hbar \frac{\partial \psi_k}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \psi_k(\mathrm{r},t) + V_{ext}(\mathrm{r},t)\psi_k(\mathrm{r},t) - eV_H(\mathrm{r},t)\psi_k(\mathrm{r},t) \qquad k=1...N$$

$$\Delta V_H = \frac{e}{\varepsilon}\sum_{j=1}^{N} p_j |\psi_j(\mathrm{r},t)|^2$$

- **They are the cornerstone of quantum mean-field dynamical theory for Coulomb-interacting particles**

Hartree's original paper

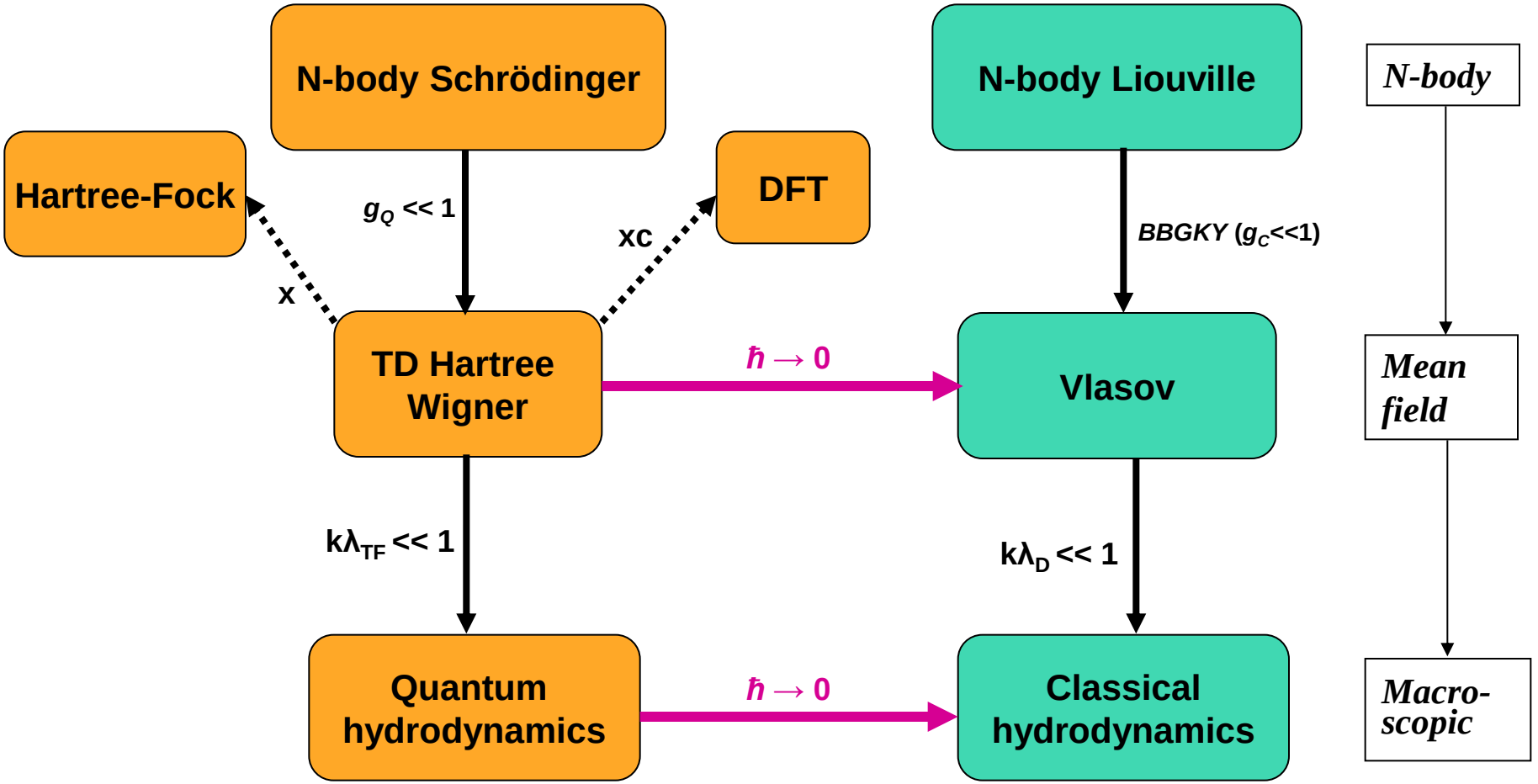
The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. By D. R. HARTREE, Ph.D., St John's College.

[*Received* 19 November, *read* 21 November, 1927.]

§ 1. *Introduction.*

On the theory of atomic structure proposed by Bohr, in which the electrons are considered as point charges revolving in orbits about the nucleus, the orbits being specified by quantum conditions, it is well known that both a qualitative and an approximate quantitative explanation of many features of the simpler optical spectra and of X-ray spectra of atoms with many electrons (e.g. Rydberg sequences in optical spectra, term magnitudes in both X-ray and optical spectra) can be given, if the assumption is made that the effects of the electrons on one another can be represented by supposing each to move in a central non-Coulomb field of force*; further, the additional concept of a spinning electron provides a similar explanation of other features of these spectra† (e.g. doublet structure of terms and magnitude of doublet separation, anomalous Zeeman effect). This assumption of a central field was admittedly a rough approximation made in the absence of any detailed ideas about the interaction between the different electrons

Synopsis of classical and quantum models



Classical mean-field models – the Vlasov equation

- Start from the Liouville equation for the 6N-dimensional distribution function

  $f^{(N)}(x_1, v_1 \ldots x_N, v_N, t)$:

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{j=1}^{N} v_j \frac{\partial f^{(N)}}{\partial x_j} + \sum_{j=1}^{N} a_j \frac{\partial f^{(N)}}{\partial v_j} = 0$$

$$a_j = a_j(x_1, \ldots, x_j) = \text{acceleration} = \frac{\text{force}}{\text{mass}}$$

Newton's eqs.

$$\frac{dx_j}{dt} = v_j$$

$$\frac{dv_j}{dt} = \frac{F_j}{m} = a_j(x_1, \ldots, x_j)$$

- Integrates over variables $x_2, v_2 \ldots x_N, v_N$ to obtain a one-body distribution

$$f^{(1)}(x_1, v_1) \equiv \int \ldots \int f^{(N)} dx_2 dv_2 \ldots dx_N dv_N$$

- But the evolution equation for $f^{(1)}$ will depend on $f^{(2)}$, which in turns depends on $f^{(3)}$, and so on → "**closure problem**"
- **BBGKY hierarchy: Born-Bogoliubov-Green-Kirkwood-Yvon**

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{j=1}^{N} v_j \frac{\partial f^{(N)}}{\partial x_j} + \sum_{j=1}^{N} a_j \frac{\partial f^{(N)}}{\partial v_j} = 0$$

$$\sum_{j=1}^{N} \int v_j \frac{\partial f^N}{\partial x_j} \, dx_2 \, dv_2 \ldots dv_N \, dx_N = v_1 \frac{\partial f^1}{\partial x_1}$$

$$\sum_{j=1}^{N} \int a_j \frac{\partial f^N}{\partial v_j} \, dx_2 \, dv_2 \ldots dx_N \, dv_N = \int a_1 \frac{\partial f^N}{\partial v_1} \, dx_2 \, dv_2 \ldots dx_N \, dv_N =$$

$$\left[\text{but:} \quad a_1 = \sum_{j=2}^{N} Q_{1j}(x_1, x_j) \right]$$

Acceleration of particle #1 caused by all other particles (j = 2,…,N)

$$= \sum_{j=2}^{N} \int Q_{1j} \frac{\partial f^N}{dv_1} \, dx_2 \, dv_2 \ldots dx_j \, dv_j \ldots dx_N \, dv_N =$$

[integrate N-2 times (except 1 and j)]

$$= \sum_{j=2}^{N} \int a_{1j}(x_1, x_j) \frac{\partial f^{(2)}}{\partial v_1} \, dx_j \, dv_j$$

where: $f^2(x_1, v_1, x_j, v_j) = \int f^N \, dx_2 dv_2 \ldots dx_{j-1} \, dv_{j-1} \, dx_{j+1} \, dv_{j+1} \ldots dx_N \, dv_N$

In summary, the Liouville equation is transformed into the following

$$\frac{\partial f^1}{\partial t} + v_1 \frac{\partial f^1}{\partial x_1} + \sum_{j=2}^{N} \int a_{1j}(x_1, x_j) \frac{\partial f^2}{\partial v_1} dx_j\, dv_j = 0$$

Fundamental hypothesis: we assume that $f^{(2)}$ can be factored → two-body correlations are neglected

$$f^2(x_1, v_1, x_j, v_j) = f^1(x_1, v_1) \times f^1(x_j, v_j)$$

$$\sum_{j=1}^{N} \int a_{1j} \frac{\partial f^1}{\partial v_1} \cdot f^1(x_j, v_j)\, dx_j\, dv_j =$$

$$\frac{\partial f_1}{\partial v_1} \cdot \sum_{j=2}^{N} \int a_{1j}(x_1, x_j)\, f^1(x_j, v_j)\, dx_j\, dv_j =$$

$N \approx N - 1$

$$\frac{\partial f^1}{\partial v_1} N \int a_1(x_1, x')\, f^1(x', v')\, dx'\, dv' = N \langle a_1 \rangle \frac{\partial f^1}{\partial v_1}$$

We write: $x_1, v_1 \longrightarrow x, v$ $\qquad f^1 \longrightarrow f(x, v)$

$$\langle a \rangle \equiv \iint a(x, x')\, f(x', v')\, dx'\, dv'$$

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial x} + N \langle a \rangle \frac{\partial f}{\partial v} = 0$$

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + N\int a(x,x')\, f(x',v')dx'\,dv'\frac{\partial f}{\partial v} = 0$$

$$a(x,x') = \frac{F}{m} = \frac{e^2}{4\pi\varepsilon m}\,\frac{1}{|x-x'|^2}$$ **Coulomb force**

In summary:

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} + \frac{e^2}{4\pi\varepsilon m}\int \frac{n(x')}{|x-x'|^2}\,dx' \cdot \frac{\partial f}{\partial v} = 0$$

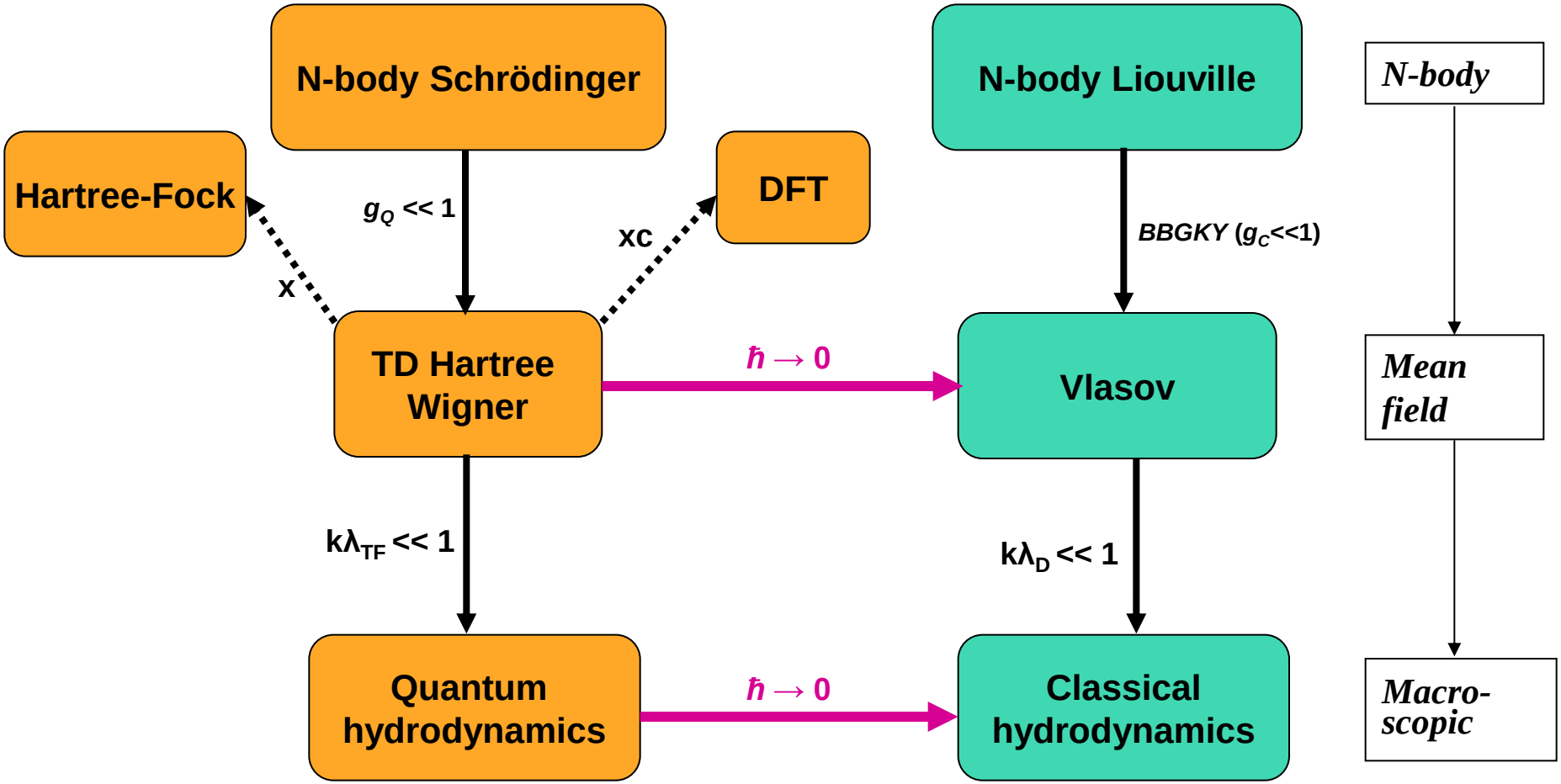
$$n(x) \equiv N\int f(x,v)\,dv$$

$$\begin{cases} \dfrac{\partial f}{\partial t} + v\dfrac{\partial f}{\partial x} + \dfrac{1}{m}\left(e\nabla V_H - \nabla V_{ext}\right)\cdot\dfrac{\partial f}{\partial v} = 0 \\ \Delta V_H = \dfrac{e}{\varepsilon}\, n(x,t) \end{cases}$$

Vlasov-Poisson system

It is the classical analog of the Hartree equations

Synopsis of classical and quantum models



From Hartree to Vlasov: Wigner functions

- Representation of quantum mechanics in the phase space
- Equivalent to more “traditional” representations: Schrödinger, Heisenberg,…
- Can deal with both pure and mixed quantum states
  - Pure state: one single wave function
  - Mixed state: N wave functions, each with occupation p_α

$$f(x,v,t) = \sum_{\alpha=1}^{N_{\rm orb}} \frac{m}{2\pi\hbar}\, p_\alpha \int_{-\infty}^{+\infty} \psi_\alpha^*\left(x+\frac{\lambda}{2},t\right)\psi_\alpha\left(x-\frac{\lambda}{2},t\right) e^{imv\lambda/\hbar}\, d\lambda$$

- Contains same information as the density matrix:

$$\rho(x,x') = \sum p_\alpha \psi_\alpha^*(x')\psi_\alpha(x)$$

$$f(x,v,t) = \frac{m}{2\pi\hbar} \int_{-\infty}^{+\infty} \rho\left(x+\frac{\lambda}{2}, x-\frac{\lambda}{2}\right) e^{imv\lambda/\hbar}\, d\lambda$$

Properties of Wigner functions

- Wigner function is real
- It can be normalized : $\int\int f\,dxdv = \sum_\alpha p_\alpha \int |\psi_\alpha|^2 dx = 1$
- By integrating over velocity, one correctly finds the spatial density:

$$n(x,t) = \int_{-\infty}^{+\infty} f(x,v,t)\; dv = \sum_{\alpha=1}^{N_{\rm orb}} p_\alpha \mid \psi_\alpha \mid^2$$

- Can be used to compute the expectation value of any variable $A(x,v)$:

$$\langle A \rangle = \frac{\int\int f(x,v)A(x,v)dxdv}{\int\int f(x,v)dxdv} = \sum_\alpha p_\alpha \langle \psi_\alpha | A | \psi_\alpha \rangle = \mathrm{Tr}(A\rho)$$

- **BUT: Wigner function can be negative!**
  - **It cannot be interpreted as a true probability distribution in the phase space**
- Wigner function must satisfy the inequality: $|f(x,p)| \le \frac{1}{\pi\hbar}$
  - (Hint: use Cauchy-Schwarz inequality in the definition of the Wigner function)
  - A manifestation of Heisenberg's uncertainty principle

Example: Gaussian wavefunction

- Pure state (minimum uncertainty packet)

$$\psi(x) = (2\pi)^{-1/4}\sigma^{-1/2}\exp[-(x-x_0)^2/4\sigma^2 + ip_0x/\hbar]$$

- The corresponding Wigner function is also a Gaussian in phase space [centered at (x_0 , p_0)]:

$$f(x,p) = \frac{1}{\pi\hbar}\exp\left[-\frac{(x-x_0)^2}{2\sigma^2} - \frac{2(p-p_0)^2\sigma^2}{\hbar^2}\right] > 0$$

- **This is the only pure-state that yields a positive Wigner function**
- For mixed states

$$f(x,p) = \frac{1}{2\pi\sigma_x\sigma_p}\exp\left(-\frac{x^2}{2\sigma_x^2} - \frac{p^2}{2\sigma_p^2}\right)$$

- The condition $|f| \le \frac{1}{\pi\hbar}$ implies $\sigma_x\sigma_p \ge \hbar/2$

Double Gaussian – entanglement

- Double Gaussian centered at $x = \pm\Delta$:

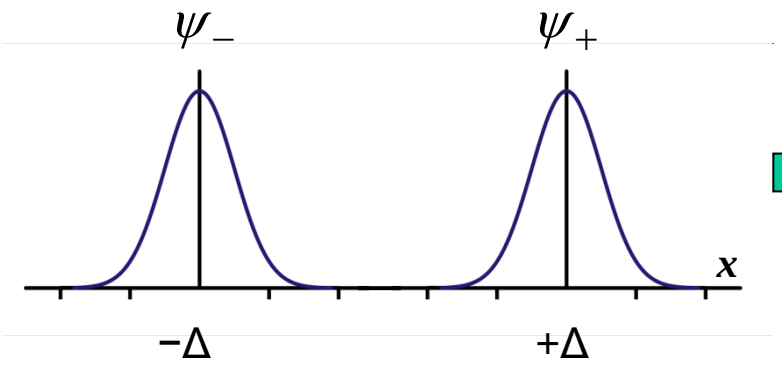
$$\psi(x) \sim \exp[-(x-\Delta)^2/4\sigma^2] + \exp[-(x+\Delta)^2/4\sigma^2] = \psi_+ + \psi_-$$

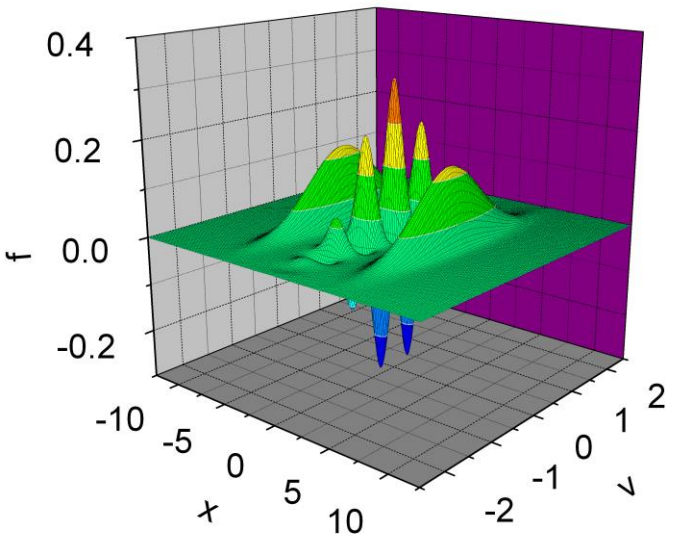
- The Wigner function displays an interference pattern around x = 0

$$f(x,p) \sim \frac{f_+ + f_-}{2} + \frac{1}{\pi\hbar}\exp\left(-\frac{x^2}{2\sigma^2} - \frac{p^2 2\sigma^2}{\hbar^2}\right)\cos\left(\frac{2p\Delta}{\hbar}\right)$$

Wigner transforms of $\psi_\pm$

Interference





Wigner evolution equation

- By using the time-dependent Schrödinger equation, one can show that the Wigner function must obey the following evolution equation

$$\frac{\partial f}{\partial t}+v\frac{\partial f}{\partial x}+\frac{m}{2i\pi\hbar^2}\int\int d\lambda\, dv' e^{im(v-v')\lambda/\hbar}\left[V_{\rm eff}\left(x+\frac{\lambda}{2}\right)-V_{\rm eff}\left(x-\frac{\lambda}{2}\right)\right]f(x,v',t)=0$$

$$V_{\rm eff} = -eV_H + V_{\rm ext} \qquad\qquad \Delta V_H = \frac{e}{\epsilon}\int f(x,v,t)\, dv$$

- Notice the nonlocal character of the interaction term
- **Equivalent to the set of N time-dependent Hartree equations**

$$i\hbar\frac{\partial\psi_k}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi_k(\mathrm{r},t) + V_{ext}(\mathrm{r},t)\psi_k(\mathrm{r},t) - eV_H(\mathrm{r},t)\psi_k(\mathrm{r},t)$$

(k=1...N)

$$\Delta V_H = \frac{e}{\varepsilon}\sum_{j=1}^{N} p_j|\psi_j(\mathrm{r},t)|^2$$

$$f(x,v,t) = \sum_{\alpha=1}^{N_{\rm orb}}\frac{m}{2\pi\hbar}\,p_\alpha\int_{-\infty}^{+\infty}\psi_\alpha^*\left(x+\frac{\lambda}{2},t\right)\psi_\alpha\left(x-\frac{\lambda}{2},t\right)e^{imv\lambda/\hbar}\,d\lambda$$

Classical limit: Wigner → Vlasov

- Expand the integral in Wigner equation in powers of $\hbar$
  - Hint: use $V_{eff}\left(x \pm \frac{\lambda}{2}\right) = V_{eff}(x) \pm \frac{\lambda}{2} V'_{eff}(x) + \frac{\lambda^2}{8} V''_{eff}(x) \pm \frac{\lambda^3}{48} V'''_{eff}(x) + \ldots$

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} - \frac{1}{m}\frac{\partial V_{\text{eff}}}{\partial x}\frac{\partial f}{\partial v} = \frac{\hbar^2}{24m^3}\frac{\partial^3 V_{\text{eff}}}{\partial x^3}\frac{\partial^3 f}{\partial v^3} + O(\hbar^4)$$

- **For $\hbar \to 0$ one recovers the classical Vlasov equation.**
- NB: this is a mathematically "tricky" limit. As $\hbar \to 0$ the Wigner function becomes more and more oscillating.
  - Example: double Gaussian

$$f(x,p) \sim \frac{f_+ + f_-}{2} + \frac{1}{\pi\hbar}\exp\left(-\frac{x^2}{2\sigma^2} - \frac{p^2 2\sigma^2}{\hbar^2}\right)\cos\left(\frac{2p\Delta}{\hbar}\right)$$

Synopsis of classical and quantum models