

Semiclassical approximations

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Other ongoing work

- Schirmer-Dreuw erroneous paper about TDDFT
 - ▶ *Comment on "Critique of ... TDDFT" [Phys. Rev. A. 75, 022513 (2007)]*, N.T. Maitra, K. Burke and R. van Leeuwen, arXiv:0710.0018., to appear in Phys Rev A
- Electron scattering from atoms using TDDFT
 - ▶ *Time-dependent Density Functional calculations of e-H scattering*, M. van Faassen, A. Wasserman, E. Engel, F. Zhang, and K. Burke, Phys. Rev. Lett. **99**, 043005 (2007).
- TDDFT for single molecule transport
 - ▶ *Density functional calculations of nanoscale conductance*, M. Koentopp, C. Chang, K. Burke, and R. Car, arXiv:cond-mat/0703591 in J. Phys C, 2008
- New way to discuss atoms in molecules
 - ▶ *Partition theory: A very simple illustration*, M.H. Cohen, A. Wasserman, and K. Burke, J. Phys. Chem. A **111**, 12447 (2007).
- Uninformed discussion of modern DFT ... *Battle of the functionals*, recent C+E News.

Outline

- 1 Review of semiclassics for N -fermions
- 2 Brief history of DFT
- 3 Finite systems in 1d
- 4 Scaling
- 5 Real world
- 6 TDDFT

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- Griffiths, *Quantum Mechanics*, about *semiclassical* approximations.

Single particle

- WKB wavefunction has first two powers of \hbar :

$$\phi_E^{WKB}(x) \approx \frac{1}{\sqrt{p(x)}} e^{i\theta(x)},$$

where ($m = e^2 = 1$):

$$p(x) = \sqrt{2(E - v(x))} \quad \theta(x) = \int_0^x dx' p(x')/\hbar.$$

- Exact for flat potential, $v(x) = 0$.
- Highly accurate for a slowly-varying potential.

N fermions

Suppose I have N (same-spin) fermions, and occupy the first N levels of the system. Is there a way to make a direct semiclassical approximation to *sums* over occupied orbitals? For example,

$$n(x) = \sum_{i=1}^N |\phi_i(x)|^2, \quad t(x) = -\frac{\hbar^2}{2} \sum_{i=1}^N \phi_i^*(x) \phi_i''(x),$$

the density and kinetic energy density ($\phi'(x) = d\phi/dx$),

$$N = \int dx n(x), \quad T = \int dx t(x),$$

Rough sums

$$n(x) \approx \int_{-\infty}^{E_F} \frac{dE}{\pi \hbar} |\phi_E(x)|^2 = \frac{k_F(x)}{\pi}, \quad k(x) = p(x)/\hbar,$$

$$t(x) \approx \int_{-\infty}^{E_F} \frac{dE}{\pi \hbar} [E - v(x)] |\phi_E(x)|^2 = \frac{\hbar^2 k_F^3(x)}{6\pi}.$$

- Both $n(x)$ and $t(x)$ are determined solely by $v(x)$ and E_F , i.e., local approximation in $v(x)$.
- Global condition to get E_F is normalization of $n(x)$:

$$\int dx n(x) = N \quad \text{or} \quad \theta_F(\infty) = N\pi.$$

Inversion

One can invert the density equation and insert into $t(x)$ equation to find:

$$t^{\text{loc}}(x) = \frac{\pi^2 \hbar^2}{6} n^3(x),$$

which is the *local density approximation* to the non-interacting kinetic energy in 1d.

Knowing $T^{\text{loc}}[n]$, one could solve the Euler equation:

$$\frac{\pi^2 \hbar^2}{2} n^2(x) + v(x) = \mu ,$$

forgetting derivation of T^{loc} .

- Continuing the expansion to higher power of \hbar , we find, e.g.,

$$n(x) = \frac{k_F(x)}{\pi} \left(1 + \frac{\hbar^2 v''(x)}{48[E_F - v(x)]^2} + \dots \right),$$
$$t(x) = \frac{\hbar^2 k_F^3(x)}{6\pi} \left(1 + \frac{\hbar^2 v''(x)}{16[E_F - v(x)]^2} + \dots \right).$$

- Notice that expansion becomes accurate when $\hbar \rightarrow 0$ or $N \rightarrow \infty$, or $v(x)$ becomes constant.
- Inversion leads to the *gradient expansion* for T :

$$T^{GE}[n] = \frac{\pi^2 \hbar^2}{6} \int dx n^3(x) - \frac{\hbar^2}{24} \int dx \frac{n'(x)^2}{n(x)} + \dots$$

Semiclassical lessons

- Semiclassical approximations are local in the potential.
- Higher orders contain gradients of the potential.
- Inversion of N -summed quantities yields gradient expansion of DFT.

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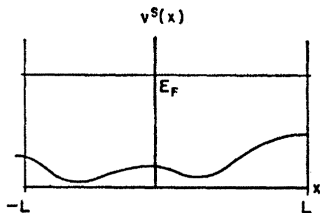
- 1926: Old DFT was Thomas-Fermi theory and extensions.
- 1965: Modern DFT begins with Kohn-Sham equations. By introducing orbitals, they get 99% of the kinetic energy right, and only need to approximate a small contribution, $E_{XC}[n]$.
- 1965: KS also suggested local density approximation (LDA) and gradient expansion approximation.

Twenty years later...

- 1988: Modern GGA's shown to give useful accuracy in chemistry.
- 1998: Nobel prize to Kohn and Pople.
- 2008: A plethora of functionals, B3LYP being the most popular. But also long history of *non-empirical* functionals, all beginning with P (for Perdew), used more in solids, including PBE.

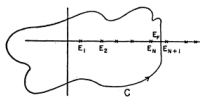
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- Simplest example: Insert hard walls at $x = 0$ and $x = L$.
- WKB traveling wavefunction no longer correct, even for flat box.
- Need to impose boundaries: choose \pm combination so that $\phi(0) = \phi(L) = 0$.
- Even yields simple condition for bound states, $\int dx p(x) = j\pi\hbar$, j an integer.
- Works well even for not-too-bumpy box or high enough, i.e., $E \rightarrow \infty$, or $\hbar \rightarrow 0$ or $v(x)$ flat.

Corrections for finite systems



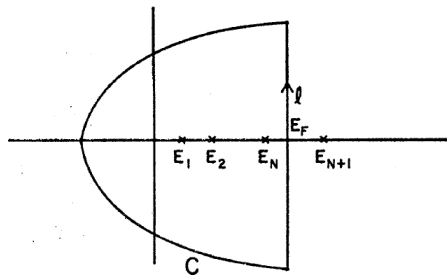
We can extract, e.g., the density from the diagonal Green's function, via

$$n(x) = \oint_C \frac{d\mathcal{E}}{2\pi i} g(x, \mathcal{E}) ,$$

where C is any contour containing just those poles at occupied levels. Usually, go above and below real axis:

$$n(x) = \int_{-\infty}^{E_F} \frac{dE}{\pi} \Im[g(x, E)] = \sum_{i=1}^N |\phi_i(x)|^2 .$$

Semiclassical Green's functions



To take maximum advantage of \hbar expansion, distort contour to keep $|\mathcal{E}| > E_F$ everywhere, because, it can be shown that

$$g(x, E) = g^{\text{semi}}(x, E) \left[1 + O\left(\frac{\hbar}{E^{3/2}} \frac{dv}{dx}\right) \right].$$

Find g^{semi} and integrate to get $n(x)$ and $t(x)$ for a box.

Semiclassical density in bumpy box

$$n^{\text{semi}}(x) = \frac{k_F(x)}{\pi} - \frac{\sin 2\theta_F(x)}{2\tau_F(L) k_F(x) \sin\left(\frac{\pi\tau_F(x)}{\tau_F(L)}\right)},$$

where E_F is found from

$$\theta_F(L) = \left(N + \frac{1}{2}\right) \pi$$

and the classical transit time at the Fermi energy is

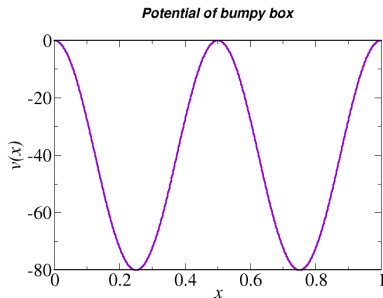
$$\tau_F(x) = \int_0^x dx' \frac{1}{k_F(x')}.$$

Properties of semiclassical density

$$n^{\text{semi}}(x) = \frac{k_F(x)}{\pi} - \frac{\sin 2\theta_F(x)}{2\tau_F(L) k_F(x) \sin\left(\frac{\pi\tau_F(x)}{\tau_F(L)}\right)},$$

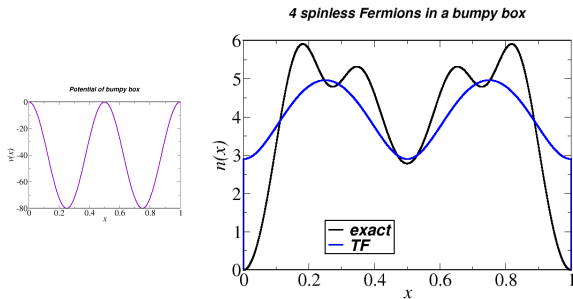
- Exact for $v = 0$, flat box.
- $\theta_F(L) = 0$ required to make $n(L)$ vanish, but does not imply normalization.
- Highly non-local functional via E_F , and integrals of local functionals $\theta_F(x)$ and $\tau_F(x)$.
- TF theory retains only first term, E_F different.
- Only valid for $E_F > v_{\text{max}}$, but works even if low-lying orbitals have turning points.

Bumpy box



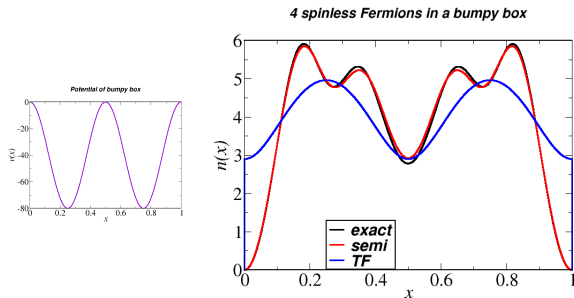
- Choose double bump: $v(x) = -80 \sin^2(2\pi x/L)$.
- Orbital energies: $-46, -42, 10, 37$, so almost degenerate first and second levels.

Density in bumpy box



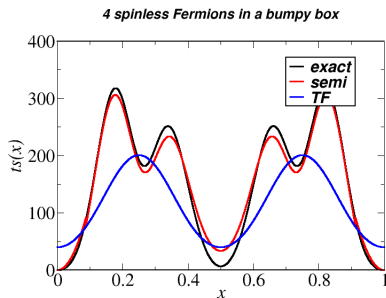
- Test quality of $n(x)$ by inserting into $T^{\text{loc}}[n]$ and find:
- Self-consistent TF (local approx) yields 115.
- Exact answer is 153.0.

Semiclassical density in bumpy box



- Norm error $< 0.2\%$.
- Test quality of $n(x)$ by inserting into $T^{\text{loc}}[n]$ and find:
- Self-consistent TF (local approx) yields 115.
- Semiclassical approximation yields 151.4.
- Exact answer is 153.0.

Kinetic energy density



- Non-zero at edges, so we smoothly interpolated to zero.
- Test quality:
- Self-consistent TF (local approx) yields 115.
- Semiclassical approximation yields 156.2.
- Exact answer is 157.2.
- Gradient correction *worsens* local approximation.

Quantum correction lessons

- Dominant terms are exactly given by *local approximation* for *all* systems as $N \rightarrow \infty$ or $v \rightarrow \text{flat}$, or $\hbar \rightarrow 0$.
- Quantum corrections are boundary-dependent and missed by traditional gradient expansion.
- Inclusion of semiclassical quantum corrections make results asymptotically exact to second-order in $1/N$, i.e., gets first three orders right.

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Potential scaling

- The formal way to think about limit:

$$v_{\text{ext}}^{\zeta}(x) = \zeta^4 v_{\text{ext}}(\zeta x), \quad N \rightarrow \zeta N .$$

Under this scaling, as $\zeta \rightarrow \infty$, our results become accurate to order in $1/\zeta^2$.

- All energies scale as

$$T(\zeta) \approx c_0 \zeta^5 + c_1 \zeta^4 + c_2 \zeta^3 + \dots , \quad \zeta \rightarrow \infty .$$

- Semiclassical approximation gets c_0 , c_1 , and c_2 right.

Density scaling

- A related limit is to scale the density:

$$n_{\zeta}(x) = \zeta^2 n(\zeta x).$$

- Under n -scaling, gradient expansion becomes accurate, but qualitatively different from v -scaling:

$$T_{\zeta} \approx c_0 \zeta^5 + c'_2 \zeta^3 + \dots, \quad \zeta \rightarrow \infty.$$

- Both yield local approximation in high-density (or potential) limit, as quantum corrections become small; so self-consistent TF theory gets exactly c_0 .
- Traditional n -gradient expansion recovers c'_2 .
- Value at $\zeta = 1$ very accurate given by v -scaling, much less accurate by n -scaling.

Scaling lessons

- Under n -scaling of any system to high-density limit, n -gradient expansion becomes exact. But this is not highly accurate at $\zeta = 1$.
- Under v -scaling to high-density limit, get quantum corrections, leading to qualitatively different expansion, which is highly accurate at $\zeta = 1$.
- Semiclassical approximation with correct boundary conditions gets v -scaling expansion right to 2^{nd} -order, and so is very accurate.

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Charge-neutral scaling

- Charge-neutral potential scaling

$$v_{\text{ext}}^{\zeta}(\mathbf{r}) = \zeta^{4/3} v_{\text{ext}}(\zeta^{1/3}\mathbf{r}), \quad N \rightarrow \zeta N.$$

- Charge-neutral density scaling

$$n_{\zeta}(\mathbf{r}) = \zeta^2 n(\zeta^{1/3}\mathbf{r}).$$

- Equivalent to changing Z for atoms, keeping neutral.
- Expansion to 2^{nd} -order is known for atoms that is highly accurate.

$$E(Z) = -0.768745 Z^{7/3} + Z^2/2 - 0.269900 Z^{5/3} + \dots, \quad Z \rightarrow \infty.$$

- Thomas-Fermi becomes exact for *all* systems in this limit (Lieb 81).

Exchange: Local approximation

- For neutral atoms, $E_x \rightarrow -0.2208 Z^{5/3}$ as $Z \rightarrow \infty$.
- Result is given exactly by local exchange applied to $n^{\text{TF}}(\mathbf{r})$.
- Thus local approximation is *universal* feature of all systems; this has nothing to do with the uniform gas.
- Correlation does *not* become local under charge-neutral scaling to high density limit, so no universality (LYP poor for uniform gas).

Exchange: Leading correction

- Next order in ζ :

$$E_x \rightarrow -d_0 Z^{5/3} - d_1 Z + \dots$$

where $d_0 = 0.22$ is given by local approximation, $d_1 = 0.195$ from numerical fitting.

- d_1 from gradient expansion $\approx d_1/2$.
- All commonly-used GGA's get d_1 about right.
- Assuming equal contributions, chose β in B88 to match:
 $\beta = 5 / [216(6\pi^5)^{1/3}] = .00378$
- Compare with .0042 from Becke's fit.

PBEsol is a trivial revision of PBE (change 2 parameters), especially designed for solid structural properties.

- Most important idea: Restore gradient expansion for exchange.
- In PBE, $\mu = 0.219$.
- In PBEsol, $\mu = 10/81 = 0.1234$.
- Means poor atomic energies, so worsens thermochemistry.

- For large neutral jellium clusters

$$E_{\text{XC}} = e_{\text{XC}}^{\text{unif}}(n) V + \sigma_{\text{XC}}(n) A + \dots$$

- $\beta = 0.046$ gives best energy (PBE had .0667).
- Consistency check: $\sigma_{\text{X}}(n)$ almost exact with restored gradient expansion for E_{X} .
- First proposed by Armiento and Mattsson (2005), whose functional gives almost identical lattice parameters.

Good results from PBEsol

- Never understood why PBE overcorrected lattice constants of LDA, leading to similar absolute error.
- PBEsol reduces error by factor of 2 or 3.
- Also gets right transition point from planar to 3D Au⁻ clusters (12 atoms).

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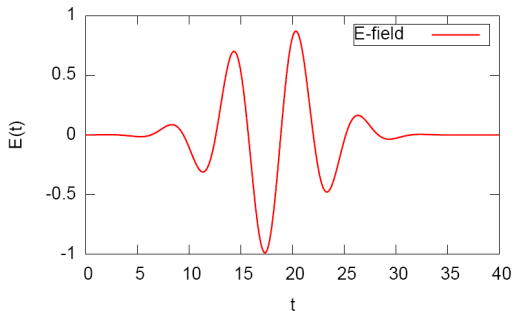
Adiabatic approximation in TDDFT

- Almost all present calculations use adiabatic approximation to XC kernel.
- ALDA can be ridiculously accurate, e.g., error in 10th Rydberg state of Be is only 4meV! (see recent work of Meta van Faassen).
- Many people focussed on going beyond adiabatic approximation, building in memory.

Adiabatic approximation in TDDFT

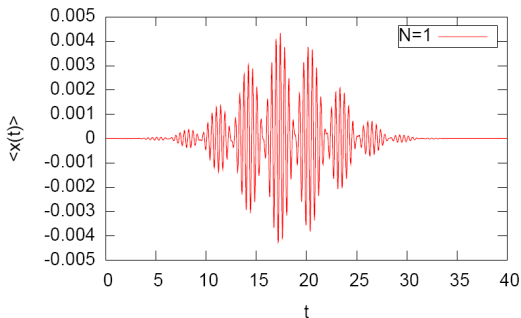
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- ALDA can be ridiculously accurate, e.g., error in 10th Rydberg state of Be is only 4meV! (see recent work of Meta van Faassen).
- Many people focussed on going beyond adiabatic approximation, building in memory.
- But why does ALDA work at all, and so damn well sometimes?

Particle in box in E-field



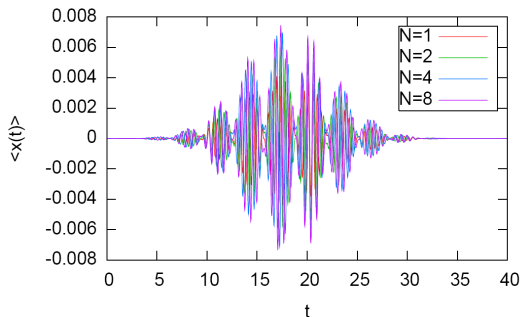
- Long slow pulse
- $L = 1$ with infinite walls

Dipole moment for one particle



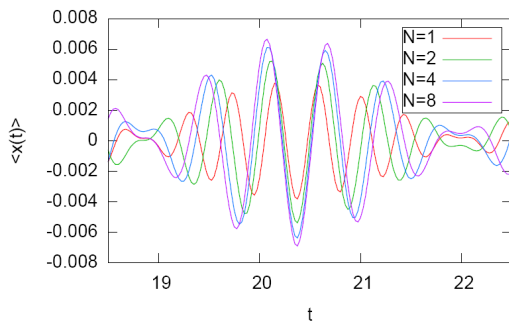
- Sloshes back and forth in response to field
- Rapid transitions between HOMO and LUMO

Dipole moment as a function of N



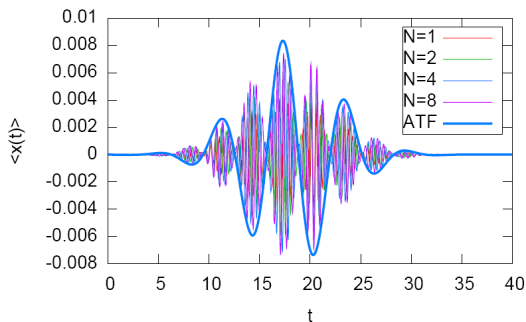
- Scale potential $v^\zeta(x, t) = \zeta^4 v(\zeta x, \zeta^3 t)$, where $\zeta = N$.
- Rescale each dipole moment back to original scale

Dipole moment as a function of N



- Zoom in on one of the pulses

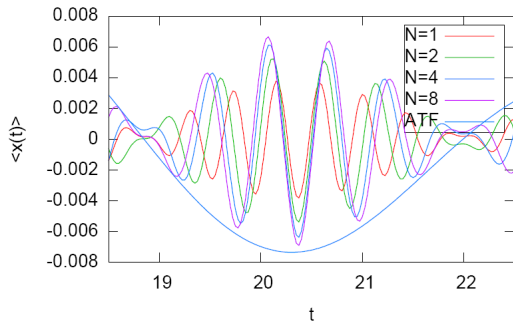
Dipole moment as a function of N and adiabatic TF



- Adiabatic TF found by solving

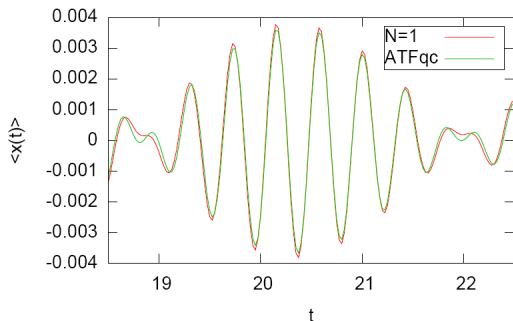
$$\frac{\pi^2}{2} n^2(x, t) + x \mathcal{E}(t) = \mu(t), \quad \int dx \mu(t) = N$$

Dipole moment as a function of N with ATF



- Zoom in on one of the pulses

Dipole moment for one particle and QC ATF



- Quantum correction simply chosen to include HOMO-LUMO transitions plus N -dependence.

Where did we learn how to do this?

Where did we learn how to do this?

PHYSICAL REVIEW

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15 MARCH 1965

Quantum Density Oscillations in an Inhomogeneous Electron Gas*

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(Received 30 October 1964)

An infinite system of electrons in its ground state, subject to a very slowly varying external potential, has slowly varying properties, and can be described by a gradient expansion theory. However, when, in addition, either (1) there is a spatially rapidly varying perturbing potential, or (2) there are regions in which the electron density drops to zero (e.g., electrons in an oscillator potential), the density and other properties of the system exhibit additional spatial oscillations, which we call quantum oscillations. An example are the Friedel oscillations in metals. In the present paper we develop a general theory of these oscillations for one-dimensional, noninteracting electrons. Illustrations are worked out which show that when the quantum oscillations are superposed on the smooth "semiclassical" results, one can obtain very accurate approximations to the exact densities.

Conclusions

- Success of DFT is based on semiclassical approximations.
- Can understand and derive better functionals from semiclassical expansions.
- Boundary conditions are all-important, hence Tower of Babel for DFT in chemistry.
- For large N potential scaling, TD becomes adiabatic.
- Perhaps ultimately replace DFT by PFT...a giant step forwards or backwards?
- Thanks to Peter Elliott, Donghyung Lee, and Attila Cangi, and NSF.
- See Phys. Rev. Lett. by Elliott et al, July, 2008.