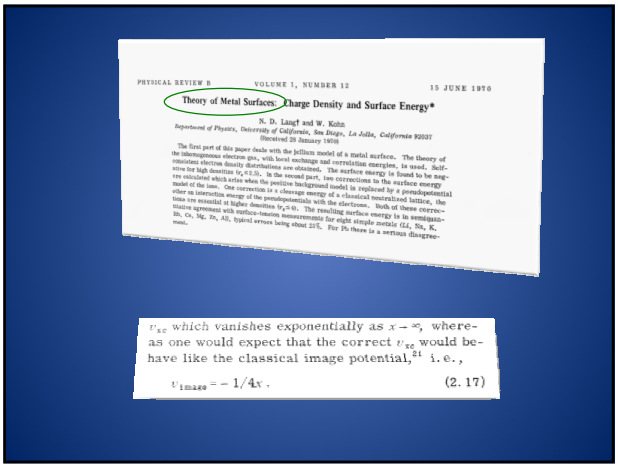
Some Lessons from the KS Exact Exchange Potential at Metal Surface

Jose Pitarke, Univ. Pais Vasco

KITP October 23, 2009



PHYSICAL REVIEW B VOLUME 1, NUMBER 12 15 JUNE 1970

Theory of Metal Surfaces: Charge Density and Surface Energy*

N. D. Lang† and W. Kohn

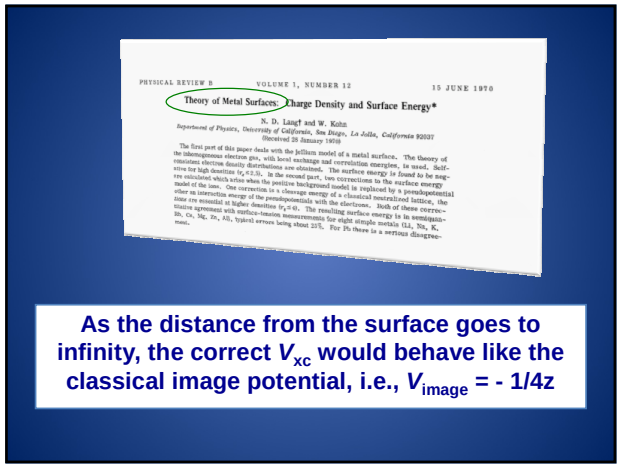
Department of Physics, University of California, San Diego, La Jolla, California 92037

Received 28 January 1970

The first part of this paper deals with the jellium model of a metal surface. The theory of the inhomogeneous electron gas, with local exchange and correlation energies, is used. Self-consistent electron density distributions are obtained. The surface energy is found to be negative for high densities ($r_s \lesssim 2.5$). In the second part, two corrections to the surface energy are calculated which arise when the positive background model is replaced by a pseudopotential model of the ions. One correction is a cleavage energy of a classical neutralized lattice, the other an interaction energy of the pseudopotentials with the electrons. Both of these corrections are essential at higher densities ($r_s \lesssim 6$). The resulting surface energy is in semiquantitative agreement with surface-tension measurements for eight simple metals (Li, Na, K, Rb, Cs, Mg, Zn, Al), typical errors being about 25%. For Pb there is a serious disagreement.

v_{xc} which vanishes exponentially as $x \to \infty$, whereas one would expect that the correct v_{xc} would behave like the classical image potential,[21] i.e.,

$$v_{\text{image}} = -1/4x\,. \qquad (2.17)$$



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As the distance from the surface goes to infinity, the correct V_{xc} would behave like the classical image potential, i.e., $V_{image} = -1/4z$

PHYSICAL REVIEW B VOLUME 20, NUMBER 8 15 OCTOBER 1979

Descriptions of exchange and correlation effects in inhomogeneous electron systems

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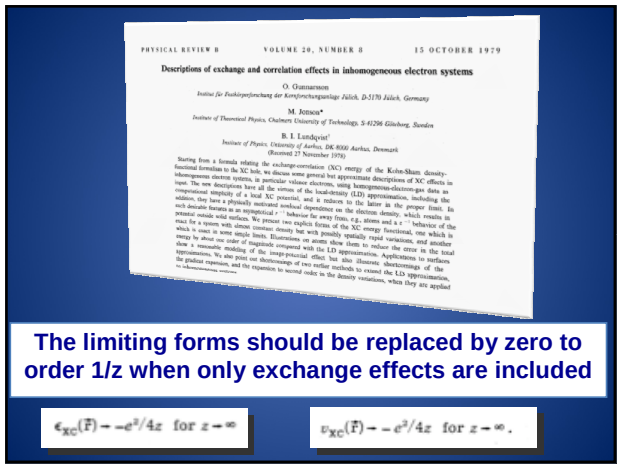
(Received 27 November 1978)

Starting from a formula relating the exchange-correlation (XC) energy of the Kohn-Sham density-functional formalism to the XC hole, we discuss some general but approximate descriptions of XC effects in inhomogeneous electron systems, in particular valence electrons, using homogeneous-electron-gas data as input. The new descriptions have all the virtues of the local-density (LD) approximation, including the computational simplicity of a local XC potential, and it reduces to the latter in the proper limit. In addition, they have a physically motivated nonlocal dependence on the electron density, which results in such desirable features as an asymptotical r^{-1} behavior far away from, e.g., atoms and a z^{-1} behavior of the potential outside solid surfaces. We present two explicit forms of the XC energy functional, one which is exact in some simple limits. Illustrations on atoms show them to reduce the error in the total energy by about one order of magnitude compared with the LD approximation. Applications to surfaces show a reasonable modeling of the image-potential effect but also illustrate shortcomings of the gradient expansion, and the expansion to second order in the density variations, when they are applied to inhomogeneous systems.

electrons. The coordinate $\vec{r}'$ of Eq. (14) will then run over the whole semi-infinite metal, replacing the limiting forms Eqs. (54) and (55) by zero to order $1/z$ when only exchange effects are included.]

$\epsilon_{xc}(\vec{r}) \to -e^2/4z$ for $z \to \infty$

$v_{xc}(\vec{r}) \to -e^2/4z$ for $z \to \infty$.



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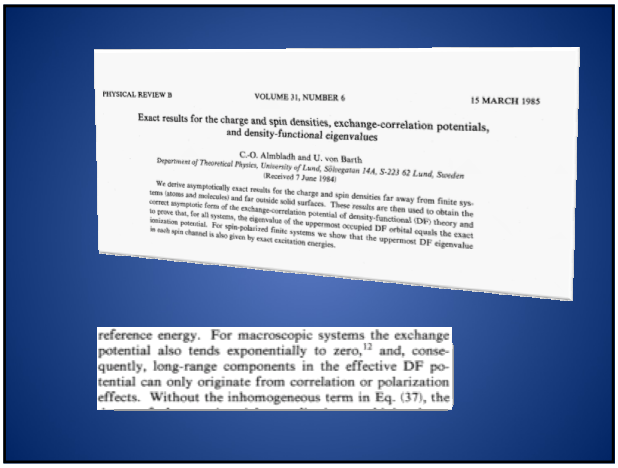


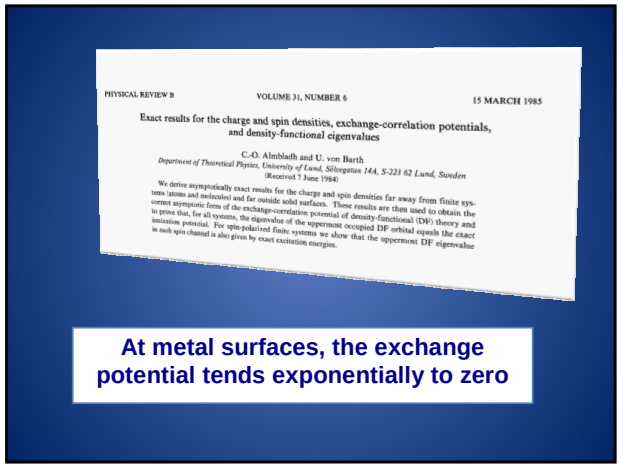
PHYSICAL REVIEW B VOLUME 31, NUMBER 6 15 MARCH 1985

Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues

C.-O. Almbladh and U. von Barth
Department of Theoretical Physics, University of Lund, Sölvegatan 14A, S-223 62 Lund, Sweden
(Received 7 June 1984)

We derive asymptotically exact results for the charge and spin densities far away from finite systems (atoms and molecules) and far outside solid surfaces. These results are then used to obtain the correct asymptotic form of the exchange-correlation potential of density-functional (DF) theory and to prove that, for all systems, the eigenvalue of the uppermost occupied DF orbital equals the exact ionization potential. For spin-polarized finite systems we show that the uppermost DF eigenvalue in each spin channel is also given by exact excitation energies.

reference energy. For macroscopic systems the exchange potential also tends exponentially to zero,[12] and, consequently, long-range components in the effective DF potential can only originate from correlation or polarization effects. Without the inhomogeneous term in Eq. (37), the



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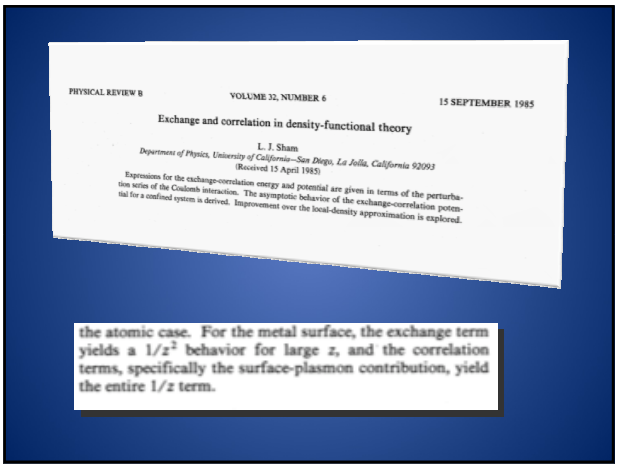
At metal surfaces, the exchange potential tends exponentially to zero



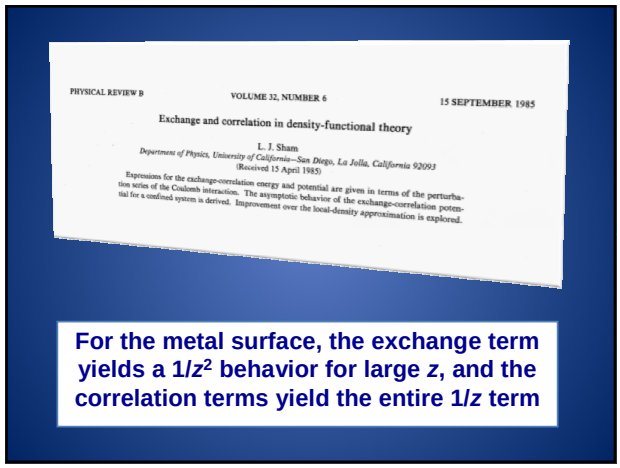
PHYSICAL REVIEW B VOLUME 32, NUMBER 6 15 SEPTEMBER 1985

Exchange and correlation in density-functional theory

L. J. Sham
Department of Physics, University of California—San Diego, La Jolla, California 92093
(Received 15 April 1985)

Expressions for the exchange-correlation energy and potential are given in terms of the perturbation series of the Coulomb interaction. The asymptotic behavior of the exchange-correlation potential for a confined system is derived. Improvement over the local-density approximation is explored.

the atomic case. For the metal surface, the exchange term yields a $1/z^2$ behavior for large z, and the correlation terms, specifically the surface-plasmon contribution, yield the entire $1/z$ term.



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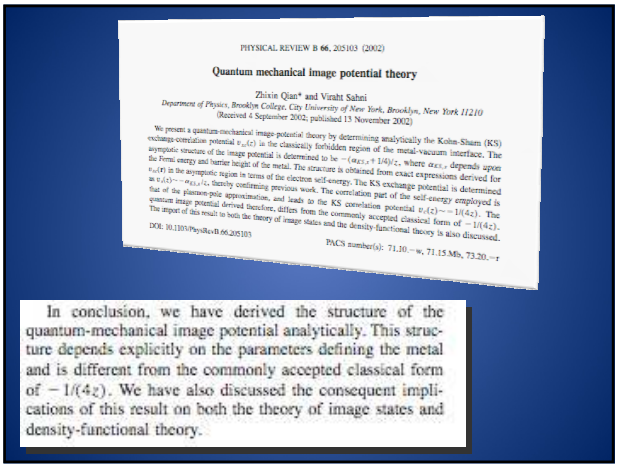


PHYSICAL REVIEW B 66, 205103 (2002)

Quantum mechanical image potential theory

Zhixin Qian* and Viraht Sahni

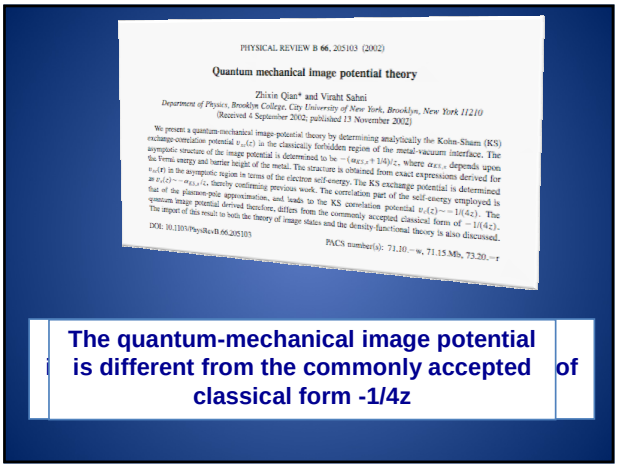
Department of Physics, Brooklyn College, City University of New York, Brooklyn, New York 11210

(Received 4 September 2002; published 13 November 2002)

We present a quantum-mechanical image-potential theory by determining analytically the Kohn-Sham (KS) exchange-correlation potential $v_{xc}(z)$ in the classically forbidden region of the metal-vacuum interface. The asymptotic structure of the image potential is determined to be $-(\alpha_{x,x}+1/4)/z$, where $\alpha_{x,x}$ depends upon the Fermi energy and barrier height of the metal. The structure is obtained from exact expressions derived for $v_{xc}(\mathbf{r})$ in the asymptotic region in terms of the electron self-energy. The KS exchange potential is determined as $v_x(z)\sim -\alpha_{x,x}/z$, thereby confirming previous work. The correlation part of the self-energy employed is that of the plasmon-pole approximation, and leads to the KS correlation potential $v_c(z)\sim -1/(4z)$. The quantum image potential derived therefore, differs from the commonly accepted classical form of $-1/(4z)$. The import of this result to both the theory of image states and the density-functional theory is also discussed.

DOI: 10.1103/PhysRevB.66.205103 PACS number(s): 71.10.−w, 71.15.Mb, 73.20.−r

In conclusion, we have derived the structure of the quantum-mechanical image potential analytically. This structure depends explicitly on the parameters defining the metal and is different from the commonly accepted classical form of $-1/(4z)$. We have also discussed the consequent implications of this result on both the theory of image states and density-functional theory.



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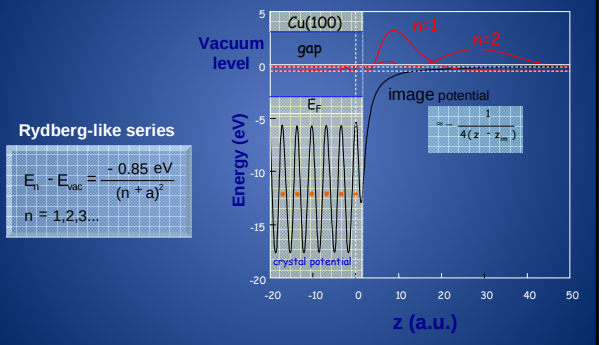
The quantum-mechanical image potential is different from the commonly accepted classical form -1/4z of

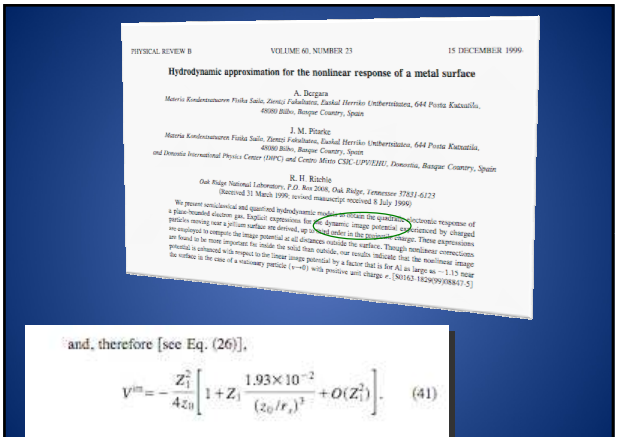
Image-potential states



Rydberg-like series

$$E_n - E_{vac} = \frac{-0.85\ \text{eV}}{(n+a)^2}$$

$n = 1,2,3...$



PHYSICAL REVIEW B VOLUME 60, NUMBER 23 15 DECEMBER 1999

Hydrodynamic approximation for the nonlinear response of a metal surface

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J. M. Pitarke

Materia Kondentsatuaren Fisika Saila, Zientzi Fakultatea, Euskal Herriko Unibertsitatea, 644 Posta Kutxatila, 48080 Bilbo, Basque Country, Spain and Donostia International Physics Center (DIPC) and Centro Mixto CSIC-UPV/EHU, Donostia, Basque Country, Spain

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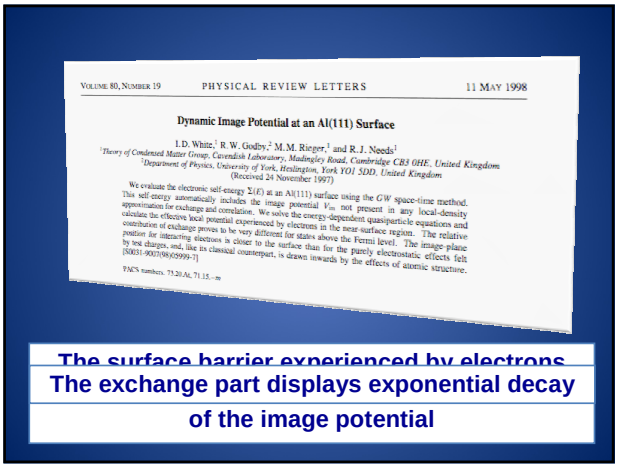
(Received 31 March 1999; revised manuscript received 8 July 1999)

We present semiclassical and quantized hydrodynamic response theories to obtain the quadratic electronic response of a plane-bounded electron gas. Explicit expressions for the dynamic image potential experienced by charged particles moving near a jellium surface are derived, up to second order in the projectile charge. These expressions are employed to compute the image potential at all distances outside the surface. Though nonlinear corrections are found to be more important for inside the solid than outside, our results indicate that the nonlinear image potential is enhanced with respect to the linear image potential by a factor that is for Al as large as −1.15 near the surface in the case of a stationary particle ($v \to 0$) with positive unit charge. [S0163-1829(99)08847-5]

and, therefore [see Eq. (26)],

$$V^{\text{im}} = -\frac{Z_1^2}{4z_0}\left[1 + Z_1\frac{1.93\times 10^{-2}}{(z_0/r_s)^3} + O(Z_1^2)\right]. \qquad (41)$$



VOLUME 80, NUMBER 19 PHYSICAL REVIEW LETTERS 11 MAY 1998

Dynamic Image Potential at an Al(111) Surface

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[1]*Theory of Condensed Matter Group, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, United Kingdom*
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(Received 24 November 1997)

We evaluate the electronic self-energy $\Sigma(E)$ at an Al(111) surface using the *GW* space-time method. This self-energy automatically includes the image potential $V_{\rm im}$ not present in any local-density approximation for exchange and correlation. We solve the energy-dependent quasiparticle equations and calculate the effective local potential experienced by electrons in the near-surface region. The relative contribution of exchange proves to be very different for states above the Fermi level. The image-plane position for interacting electrons is closer to the surface than for the purely electrostatic effects felt by test charges, and, like its classical counterpart, is drawn inwards by the effects of atomic structure.

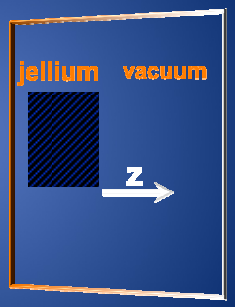
PACS numbers: 73.20.At, 71.15.–m

The surface barrier experienced by electrons

The exchange part displays exponential decay of the image potential

$$E_{xc}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \varepsilon_{xc}(\mathbf{r})$$

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$



KS xc OEP potential

$$\int_0^{k_F} (k_F^2 - k^2)\Psi_k^*(z)\xi_k(z)\, dk \;+\; \text{c. c.} = 0$$

$$V_{xc}(z) = V_{xc}^{\rm KLI}(z) + V_{xc}^{\rm Shift}(z)$$

KS xc OEP potential

$$V_{xc}^{\rm KLI}(z) = \int_0^{k_F} \frac{|\xi_k(z)|^2}{2\pi^2 n(z)} \left[u_{xc}^{k}(z) + \Delta\overline{V}_{xc}^{\,k}\right] \widetilde{dk}$$

$$V_{xc}^{\rm Shift}(z) = \int_0^{k_F} \frac{[\Psi_k(z)\xi_k(z) + \Psi_k'(z)\xi_k'(z)]}{2\pi^2 n(z)}\, \widetilde{dk}$$

KS exact-exchange asymptotics

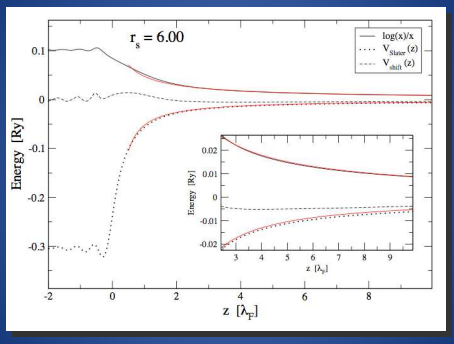
$$V_x^S(z\to\infty) = -\frac{e^2(\pi+2\alpha\ln\alpha)}{\pi(1+\alpha^2)}\frac{1}{z}$$

$\xi_k(z\to\infty)\to\xi_{k_F}(z\to\infty)e^{-\alpha z\Delta k}$

$n(z\to\infty)\to\frac{3\bar{n}}{4(\alpha k_F z)^2}|\xi_{k_F}(z\to\infty)|^2$

$$V_x^\Delta(z\to\infty) = \frac{e^2}{2\pi\alpha z}[\ln(\alpha k_F z)+C]$$

Horowitz, Proetto, and JMP (unpublished)



Horowitz, Proetto, and JMP (unpublished)

Adiabatic connection for e_xc(z)

- Pair distribution function

  $g(\mathbf{r},\mathbf{r}')$
- xc hole density

  $n_{xc}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}')\,[g(\mathbf{r},\mathbf{r}')-1]$
- xc energy per particle

  $$\varepsilon_{xc}(\mathbf{r}) = \frac{1}{2}\int d^3\mathbf{r}'\,\frac{\bar{n}_{xc}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$E_{xc}[n] = \int d\mathbf{r}\, n(\mathbf{r})\,\varepsilon_{xc}(\mathbf{r})$$

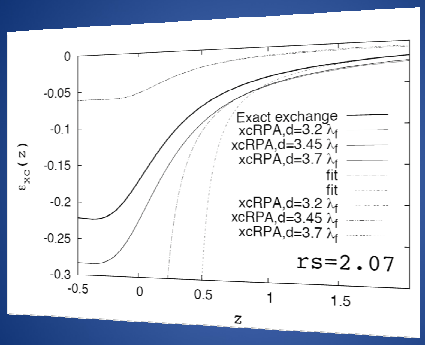
$$V_{xc}(\mathbf{r}) = \varepsilon_{xc}(\mathbf{r}) + \int d\mathbf{r}'\, n(\mathbf{r}')\frac{\delta\varepsilon_{xc}(\mathbf{r}')}{\delta n(\mathbf{r})}$$

$$V_{xc}(\mathbf{r}) = 2\,\varepsilon_{xc}(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}_1\, n(\mathbf{r}_1)\int d\mathbf{r}_2\frac{n(\mathbf{r}_2)}{\mathbf{r}_1-\mathbf{r}_2}\frac{\delta g_{xc}(\mathbf{r}_1,\mathbf{r}_2)}{\delta n(\mathbf{r})}$$

Fluctuation-dissipation

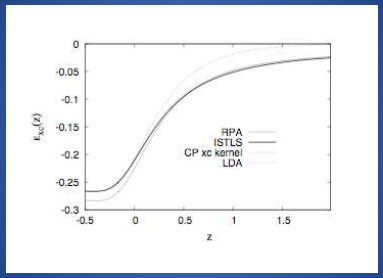
$$n_{xc}^{\lambda}(\mathbf{r},\mathbf{r}') = \frac{1}{n(\mathbf{r})}\left[-\frac{1}{\pi}\int_0^{\infty} d\omega\, \chi^{\lambda}(\mathbf{r},\mathbf{r}';i\omega) - n(\mathbf{r})\,\delta(\mathbf{r}-\mathbf{r}')\right]$$

- TDDFT: RPA, CP
- ISTLS



$$\varepsilon_{xc} \to -\frac{\alpha}{(z-z_0)}$$

Constantin and JMP (unpublished)



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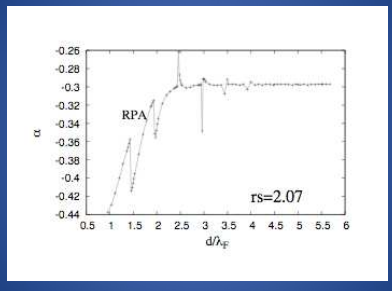

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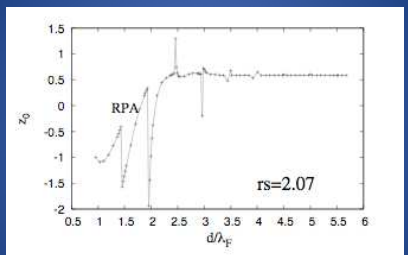

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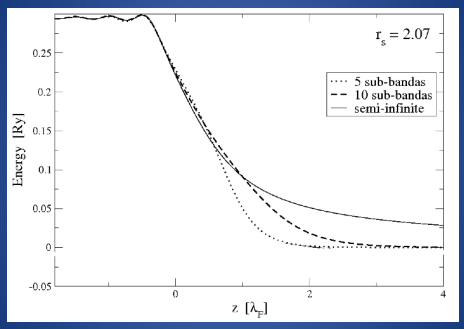

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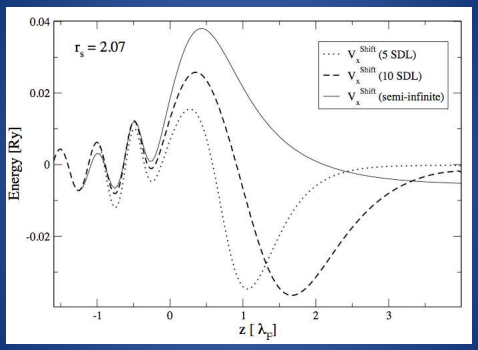

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