

## Free Electron Gas II

### Thomas-Fermi Kinetic Energy

solutions:  $\psi_i = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}$

(in a large box of volume  $V$ , and lengths  $L_x, L_y, L_z$ )

Solutions must have nodes at boundaries  $L_x, L_y, L_z$ :

$$k_\alpha = \frac{2\pi n_\alpha}{L_\alpha} \quad \text{are the allowed values of } k$$

$n_\alpha$  integers

Allowed wave numbers, 1 per  $\delta k_x \delta k_y \delta k_z = \frac{2\pi}{L_x} \frac{2\pi}{L_y} \frac{2\pi}{L_z} = \frac{(2\pi)^3}{V}$

Density of states  $\frac{V}{(2\pi)^3}$

KE of each state is  $\int \frac{\hbar^2 \mathbf{v}^2}{2m} \psi_i^* \psi_i = \frac{\hbar^2 k^2}{2m}$

So fill states in a sphere upto  $k_F$

$$N = \rho V = \frac{4}{3} \pi k_F^3 \cdot 2 \cdot \frac{V}{(2\pi)^3}$$

$$k_F = (3\pi^2 \rho)^{1/3}$$

Average KE:  $\left\langle \frac{\hbar^2 k^2}{2m} \right\rangle = \frac{\int_0^{k_F} \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk}{\int_0^{k_F} 4\pi k^2 dk} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m}$

$$KE_{TF} = \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3} \rightarrow \frac{3}{10} (3\pi^2 \rho)^{2/3} \text{ in Hartrees}$$

## Hartree Potential

Solve Poisson's equation.

$$\nabla^2 V_H(r) = -4\pi \rho(r)$$

$$U(r) = r V_H(r)$$

$$\frac{d^2}{dr^2} U(r) = -4\pi r \rho(r)$$

If you normalize  $\int dr U^2(r) = 1$

$$U''(r) = -\frac{u^2(r)}{r}$$

$$U(0) = 0 \quad V_H'(r_{\max}) = \frac{g_{\max}}{r_{\max}^2}$$

$$g_{\max} = \int_0^{r_{\max}} dr u^2(r)$$

Integrate outward  $U(0) = 0 \quad U(h) = h$

Homogeneous solution:  $U(r) = \alpha r \quad U''(r) = 0$

So add  $\alpha r$  to solution w/  $\alpha$  chosen to make  $U(r_{\max}) = g_{\max}$

What are the eigenvalues in DFT?

They are not excitation energies.

One can show (Perdew + Zunger, 1981) that

$$\epsilon_{\alpha} = \frac{\partial E}{\partial f_{\alpha}}$$

where  $f_{\alpha}$  is the occupation of state  $\alpha$ .

Band gap problem:

Gaps are too small, and sometimes zero for insulators.

Band gap is the difference in ground state energy for the  $N$ -electron and  $N+1$  electron system, so it seems the exact DFT should give this energy difference correctly (though not necessarily for the eigenvalues).

(Nevertheless, there is an argument based on defects that the eigenvalues should also give the correct gap.)

## Excitation Energies in DFT

Band gap  $E_g = E(N+1) - E(N)$

$$E_g = \underbrace{E_{\text{conduction band minimum}}^N}_{\text{conduction band minimum}} - \underbrace{E_{\text{valence band max}}^N}_{\text{valence band max}} + \Delta V_{xc}$$

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N)$$

$$\neq \epsilon_{N+1}(N) - \epsilon_N(N)$$

$$\Delta V_{xc} = \epsilon_{N+1}(N+1) - \epsilon_{N+1}(N)$$

Much more can be said...

Another point: excitation energies can all be obtained by applying a time varying potential and looking for resonances.

# Perdew Burke + Ernzerhof (PBE) GGA Generalized Gradient Approximation

- 1) non-empirical
- 2) universality
- 3) simplicity
- 4) accuracy

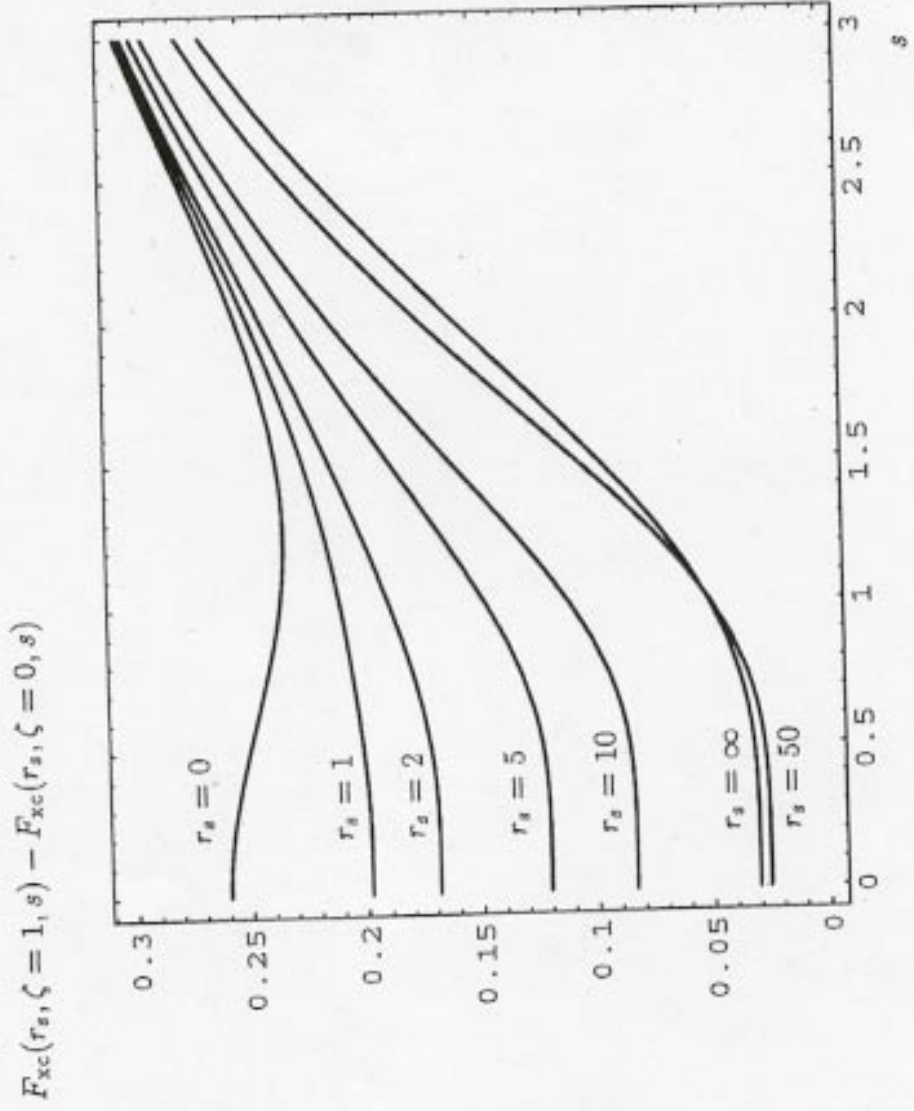
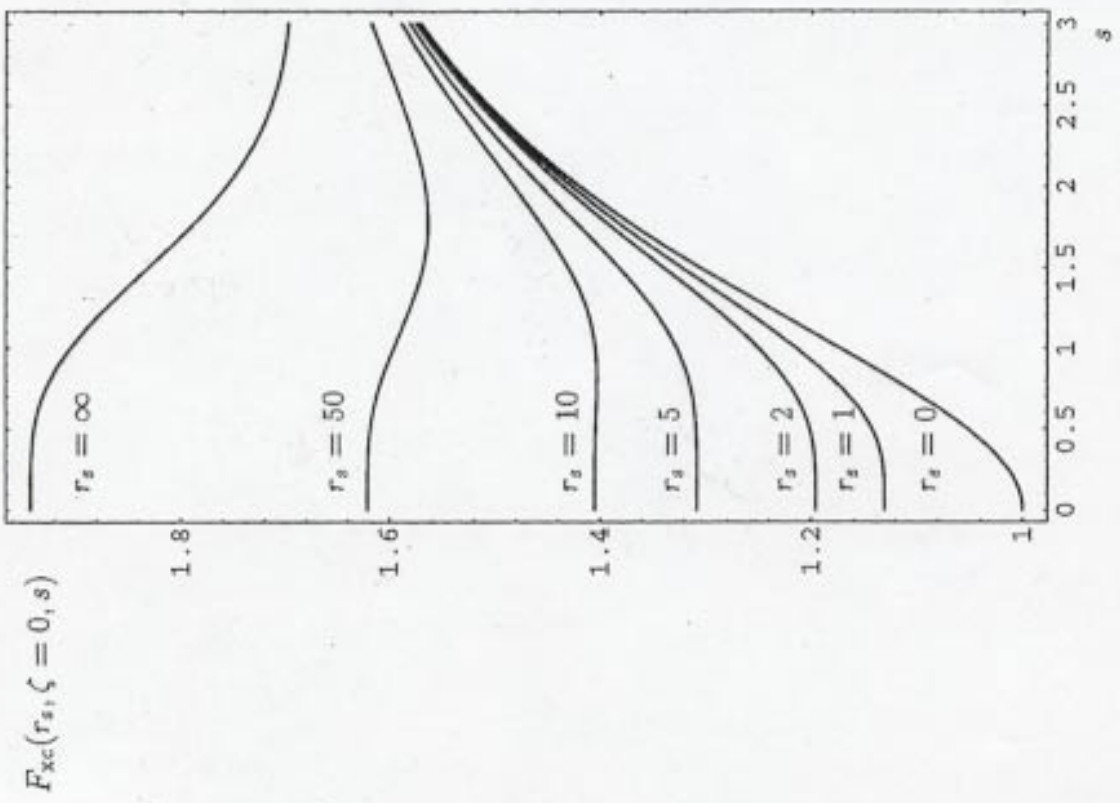
- A) Keep everything that LDA does right.  
scaling, xc hole = -1, bounds,  $r_s$  limits
- B) reduce to LDA for  $\nabla\rho \rightarrow 0$

$$E_{xc}^{GGA}[\rho_{\uparrow}, \rho_{\downarrow}] = \int d^3r \rho e_x F_{xc}(r_s, \zeta, s)$$

$$r_s = \left(\frac{4}{3}\pi\rho\right)^{-1/3} \quad \text{avg dist between electrons}$$

$$\zeta = \frac{\rho_{\uparrow} - \rho_{\downarrow}}{\rho}$$

$$s = \frac{|\nabla\rho|}{2k_F\rho} = \frac{|\nabla\rho|}{2\left(\frac{3\pi}{4}\right)^{1/3}\rho^{4/3}} = \frac{3}{2}\left(\frac{4}{9\pi}\right)^{1/3}|\nabla r_s|$$



## Notes on atomic calculations

Central field approximation (not made in basis set calculations if potential is also represented by  $f_{lm}(r)$ )

$$\psi_i^{lm}(r) = \frac{u_i^l}{r} Y_{lm}(\theta, \varphi)$$

$$V = V(r) \quad \text{No } m \text{ dependence of } u.$$

(OK for closed shells)

But for open shell systems should have a non-spherical density + potential, and radial part will have  $m$  dependence (few implement)

# Atoms (more)

Find eigen energies

$E, E_{high}, E_{low}$

Initial guess input

$$E_{high} = 0$$

$$E_{low} = 10 \times E$$

Find classical turning point at  $E$  (largest one)  
Integrate outward to  $R_{turn}$   
Count nodes

Correct # nodes  $n - l - 1$ ?

too many nodes?  $E$  too high, bisect  $E, E_{low}$   
(set  $E_{high} = E$ )

too few nodes?  $E$  too low, bisect  $E, E_{high}$   
(set  $E_{low} = E$ )

Check log derivative, negative

Integrate inward

Difference in log derivative  $D = \frac{u'_{out}}{u_{out}} - \frac{u'_{in}}{u_{in}}$   
small?

$D > 0$   $E$  is too low  $E_{low} = E$

$D < 0$   $E$  is too high  $E_{high} = E$

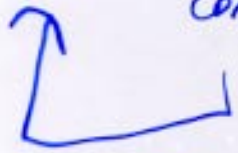
Bisection or secant method for  $E$

Integrate out

Do for all states

## Atoms (contd)

Compute charge density  
compute potential



converged?

total E etc.

$$V(r) \rightarrow -\frac{Z}{r} \text{ as } r \rightarrow 0$$

$$V(r) \rightarrow 0 \text{ as } r \rightarrow \infty$$

# Self interaction Corrections SIC

Main error in LDA and GGA

$$U[\rho] = \frac{1}{2} \int d^3r \int d^3r' \frac{\rho(r)\rho(r')}{|r-r'|}$$

Includes interaction of  $e^-$  with itself.

This should be cancelled by  $E_x$ , but doesn't happen in LDA, GGA, etc.

SIC: impose  $U[\rho_{\alpha\sigma}] + E_{xc}[\rho_{\alpha\sigma}] = 0$

$$\rho_{\alpha\sigma} = f_{\alpha\sigma} |\psi_{\alpha\sigma}|^2 \quad E_c[\rho_{\alpha\sigma}] = 0$$

$$E_{xc}^{SIC} = E_{xc}^{LDA}[\rho_{\uparrow}, \rho_{\downarrow}] - \sum_{\alpha\sigma} \left\{ U[\rho_{\alpha\sigma}] + E_{xc}^{LDA}[\rho_{\alpha\sigma}] \right\}$$

Note: near cancellation already in LDA:

$$U[\rho] \approx 1.092 N^{2/3} \int d^3r \rho^{4/3}(r)$$

$$E_x^{LSDA}[\rho_{\uparrow}, \rho_{\downarrow}] = -0.9305 \int d^3r [\rho_{\uparrow}^{4/3} + \rho_{\downarrow}^{4/3}]$$

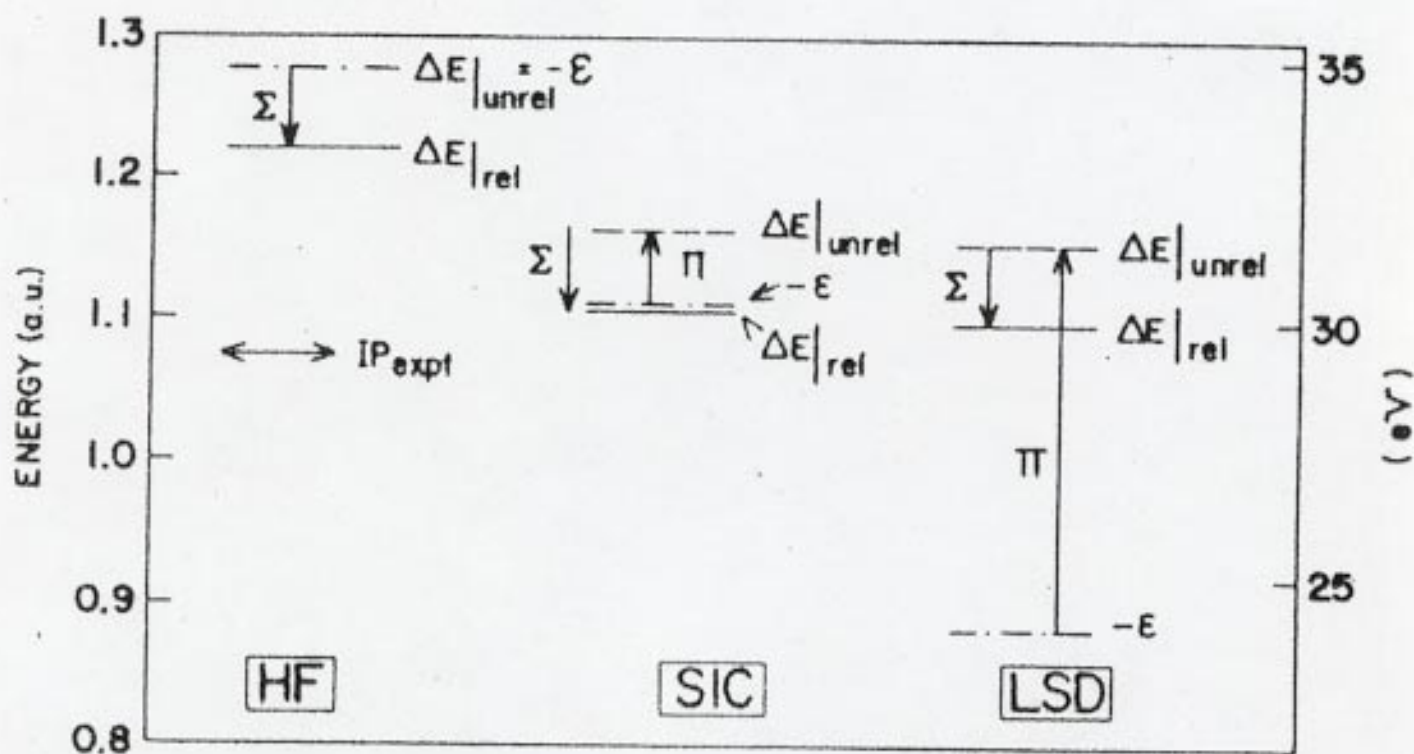


FIG. 3. Relationships between the orbital-energy eigenvalue  $\epsilon$ , the unrelaxed energy difference  $\Delta E|_{unrel}$ , and the relaxed energy difference  $\Delta E|_{rel}$  upon removal of an electron, in the HF, SIC-LSD, and LSD approximations. In the example shown here, the electron is removed from the 3s orbital in atomic Ar. The relaxation energy  $\Sigma$  has been taken from HF calculations.

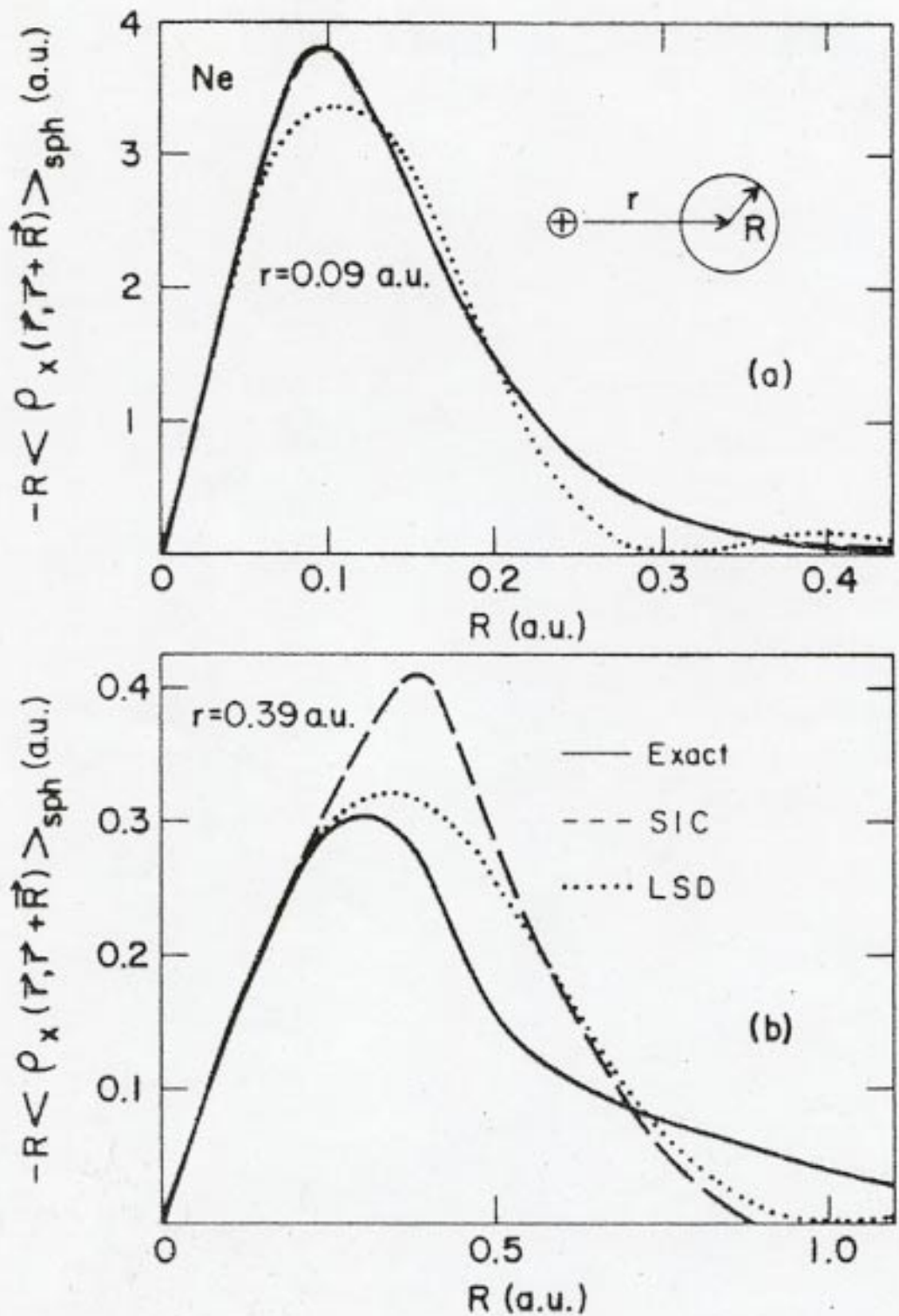


FIG. 2. Spherical average of the neon exchange hole times  $R$  for (a)  $r = 0.09$  a.u. and (b)  $r = 0.39$  a.u. The full, dashed, and dotted curves are the exact, SIC-LSD and LSD results, respectively. In part (a), the SIC-LSD curve is almost indistinguishable from the exact one.

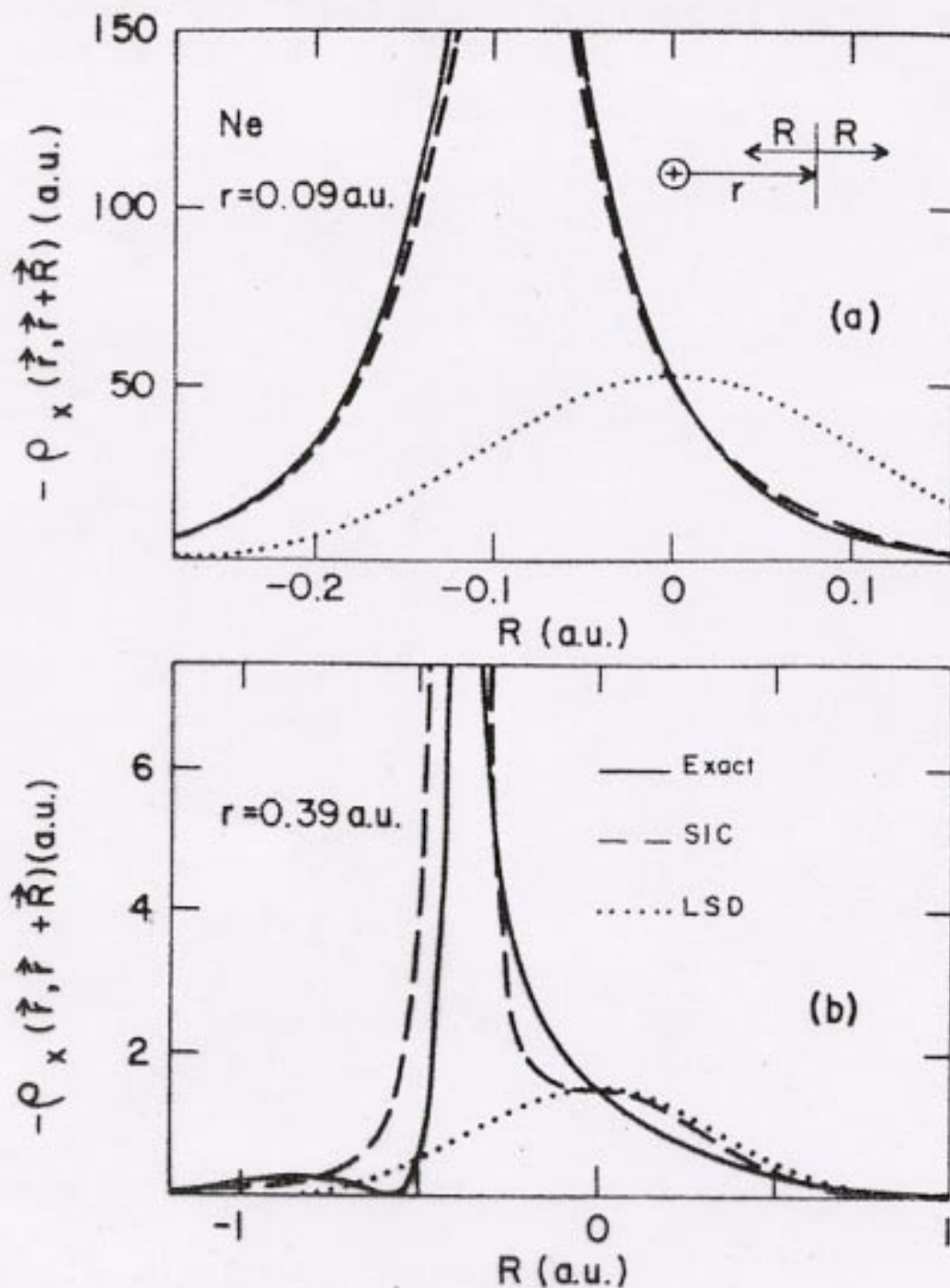


FIG. 1. Exchange hole about an electron located at distance  $r$  from the nucleus in the neon atom. The full curves are exact, while the dashed and dotted curves represent the SIC-LSD and LSD approximations,