Neutralization of H^- near metal vicinal surfaces

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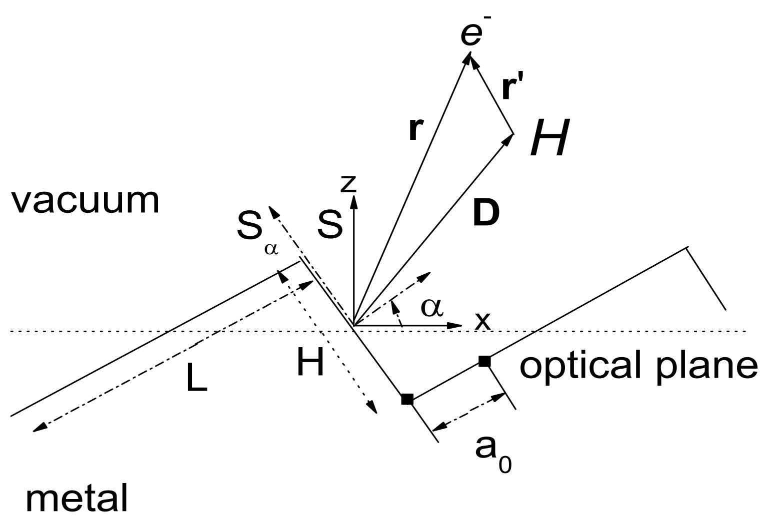
Ion-surface scattering scenario



The electronic Hamiltonian in B.O approximation, $(e = \hbar = m_e = 1)$

$$H = -\frac{1}{2}\nabla^2 + V_{\mathrm{e-surf}}(\mathbf{r}) + V_{\mathrm{e-H}}(\mathbf{r};\mathbf{D}),$$

Schrödinger equation for the electronic motion

$$i\frac{\partial}{\partial t}\Psi(t) = H\Psi(t), \quad \Psi(0) = \psi_{ion}$$

Transition amplitude

$$A(t;\mathbf{D}) = \langle \Psi(t;\mathbf{D}) | \Psi(0) \rangle$$

Projected density of states

$$\rho(E;\mathbf{D}) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt e^{iEt} A(t;\mathbf{D})$$

For isolated resonances

$$\rho = \rho_0 + A\frac{\Gamma/2}{(E-E_r)^2 + \Gamma^2/4}$$

Ion-survival probability (rate equation)

$$P = e^{-\int_{-\infty}^{\infty} dt \ \Gamma(\mathbf{D}(t))}$$

Collision energy $E = 1$ keV, broken-straight-line trajectories

$$\mathbf{D}(t) = \mathbf{D}_{\text{cls}} + \mathbf{v}_i(t_0 - t), \quad t < t_0$$

$$\mathbf{D}(t) = \mathbf{D}_{\text{cls}} + \mathbf{v}_r(t - t_0), \quad t \geq t_0$$

$$|\mathbf{v}_i| = |\mathbf{v}_r|$$

$$\mathbf{D}(t) = (D_{\text{par}}(t), D_{\text{nor}}(t)), \quad \mathbf{v} = (v_{\parallel}, v_{\perp})$$

Effective potentials

Electron-hydrogen interaction potential in 3D

$$U(r') = -\exp(-2r')/r' - (4.5/2r'^4)\exp(-2.547/r'^2),$$

In 2D

$$V_{\mathrm{e-H}} = \frac{1.107\ U}{\sqrt{0.1417\ U^2 + 1}}$$

Electron-surface interaction potential

$$V_{\mathrm{e-surf}}(\mathbf{r}) = \phi(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r})$$

Thomas-Fermi-von Weizsäcker model.

$$E[n] = T_s[n] + E_{\rm xc}[n] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' n(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r}') - \int d\mathbf{r}\int d\mathbf{r}' n_J(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}n(\mathbf{r})$$

$$T_s[n] = \int d\mathbf{r}\left(\frac{3}{10}(3\pi^2)^{2/3}n^{5/3}(\mathbf{r}) + \frac{\lambda_w}{8}\frac{|\nabla n|^2}{n}\right)$$

$$E_{\rm xc}[n] = -\int d\mathbf{r}\ \left(\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} n^{4/3}(\mathbf{r}) + \frac{0.44n(\mathbf{r})}{7.8+(3/4\pi n(\mathbf{r}))^{1/3}}\right)$$

Euler-Lagrange equation for the static electron density

$$\frac{\delta E[n]}{\delta n(\mathbf{r})} - \mu = 0$$

$$V_{\rm xc}(\mathbf{r}) = \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}, \quad \phi(\mathbf{r}) = \int d\mathbf{r}'\frac{n(\mathbf{r}')-n_J(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Substitution $n(\mathbf{r}) = \psi_w^2(\mathbf{r}), \Rightarrow$

$$\left(-\frac{\lambda_w}{2}\nabla^2 + v_{\rm eff}(\mathbf{r})\right)\psi_w(\mathbf{r}) = \mu\psi_w(\mathbf{r}), \quad \lambda_w = 1/4$$

$$\begin{aligned} v_{\rm eff}(\mathbf{r}) &= \phi(\mathbf{r}) + \frac{1}{2}(3\pi^2)^{2/3}\psi_w^{4/3}(\mathbf{r}) - \left(\frac{3}{\pi}\right)^{1/3}\psi_w^{2/3}(\mathbf{r}) - \\ &- 0.44\psi_w^{2/3}(\mathbf{r})\frac{7.8\psi_w^{2/3}(\mathbf{r}) + (4/3)(3/4\pi)^{1/3}}{(7.8\psi_w^{2/3}(\mathbf{r}) + (3/4\pi)^{1/3})^2}. \end{aligned}$$

$$\nabla^2\phi(\mathbf{r}) = -4\pi(\psi_w^2(\mathbf{r}) - n_J(\mathbf{r})), \quad n_J = n_{\rm bulk}\theta(\xi(x,y)-z)$$

Characteristic length-scales

Fermi wavelength λ_F and Wigner-Seitz radius r_s

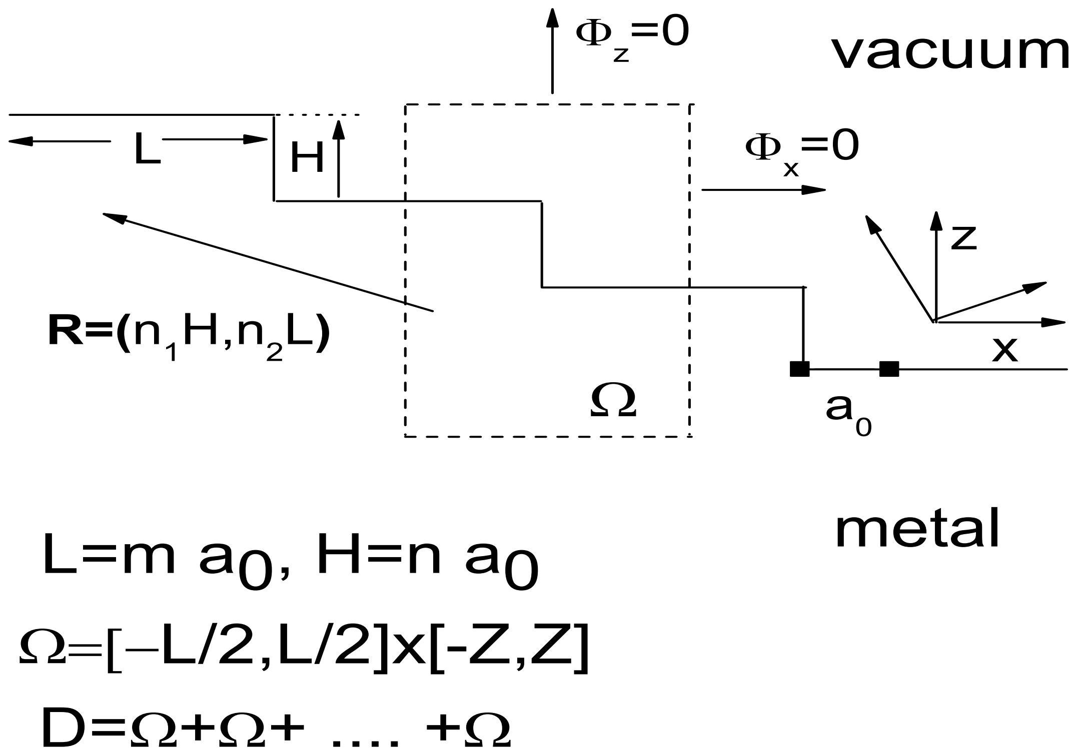
$$\lambda_F = 2\pi/k_F, \quad k_F = (3\pi^2 n_{\rm bulk})^{1/3}, \quad r_s = \left(\frac{3}{4\pi n_{\rm bulk}}\right)^{1/3}$$

Thomas-Fermi screening length $l_{\rm TF}$

$$l_{\rm TF} = \sqrt{\frac{E_F}{6\pi n_{\rm bulk}}}, \quad E_F = k_F^2/2$$

metal	r_s	$n_{\rm bulk}$	$l_{\rm TF}$	λ_F
Al	2	0.0298	0.90	6.55
Cu	3	0.0088	1.11	9.82
Na	4	0.0037	1.28	13.10
K	5	0.0019	1.43	16.37

Numerical method



$$\Omega = [-L/2, L/2] \times [-Z, Z].$$

$$\mathbf{e}_x \cdot \nabla\psi_w = 0,\ \mathbf{e}_x \cdot \nabla\phi = 0, \quad x = \pm L/2,\ \forall z \in \Omega$$

$$\psi_w(x, -Z) = \sqrt{n_b}, \quad \psi_w(x, Z) = 0, \quad \forall x \in \Omega$$

$$\mathbf{e}_z \cdot \nabla\phi = 0, \quad z = \pm Z, \quad \forall x \in [-L/2, L/2].$$

$$\psi_w(\mathbf{r}') = \psi_w(T_{\mathbf{R}}^{-1}\mathbf{r}), \quad \phi(\mathbf{r}') = \phi(T_{\mathbf{R}}^{-1}\mathbf{r}).$$

$$\psi_w(\mathbf{r}) \leftarrow \psi_w(R_\alpha^{-1}\mathbf{r}), \quad \phi(\mathbf{r}) \leftarrow \phi(R_\alpha^{-1}\mathbf{r}).$$

$$\Omega^h = (\delta_x, \delta_z)$$

Relaxation method for the NLSE

$$\psi^h(t+\delta t) = \psi^h(t) + \left(-\frac{\lambda_w}{2} L^h + v_{\text{eff}}^h - \mu\right) \psi^h(t) \delta t,$$

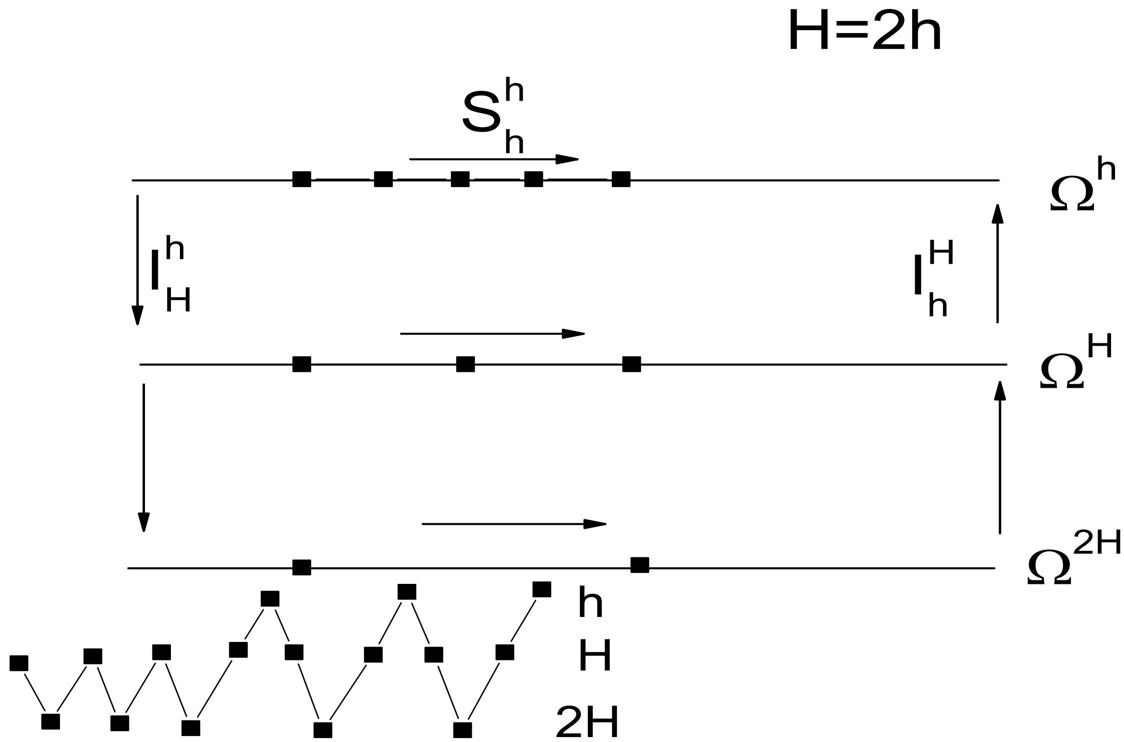
$$\psi^h(0) = \psi_0, \quad \delta t < \frac{1}{4} \min(\delta_x^2, \delta_z^2),$$

$$L^h \psi^h = \frac{1}{\delta_x^2}(\psi_{i+1,j} - 2\psi_{i,j} + \psi_{i-1,j}) + \frac{1}{\delta_z^2}(\psi_{i,j+1} - 2\psi_{i,j} + \psi_{i,j-1})$$

$$v_{\text{eff}}^h = \phi^h + v_{\text{xc}}(\psi^h) + \frac{5}{3}(\psi^h)^{4/3}$$

$$\mu = \frac{5}{3}(\psi_{\text{bulk}})^{4/3} + v_{\text{xc}}(\psi_{\text{bulk}}) + \phi_{\text{bulk}}$$

Multigrid method for the Poisson's equation



$$L^h \phi^h = -4\pi[(\psi^h)^2 - n_J^h] = f^h$$

$$e^h = \phi^h - \tilde{\phi}^h, \quad r^h = f^h - L^h \tilde{\phi}^h, \quad L^h e^h = r^h$$

Coarse-grid correction

$$r^H = I_h^H r^h, \quad L^H e^H = r^H, \quad e^H = (L^H)^{-1} r^H, \quad \tilde{\phi}^h \leftarrow \tilde{\phi}^h + I_H^h e^H$$

Restriction and interpolation operators

$$I_h^H : \Omega^h \to \Omega^H, \quad I_H^h : \Omega^H \to \Omega^h, \quad H = 2h$$

$$I_h^H = \left\{ \begin{array}{ccc} 1/4 & 1/2 & 1/4 \\ 1/2 & 1 & 1/2 \\ 1/4 & 1/2 & 1/4 \end{array} \right\}, \quad I_H^h = \left\{ \begin{array}{ccc} 0 & 1/8 & 0 \\ 1/8 & 1/2 & 1/8 \\ 0 & 1/8 & 0 \end{array} \right\}$$

Relaxation $S : \Omega^h \to \Omega^h$

$$S : \ \tilde{\phi}_{i,j} \leftarrow \left(f_{i,j} - \frac{1}{\delta_x^2}(\tilde{\phi}_{i-1,j} + \tilde{\phi}_{i+1,j}) - \frac{1}{\delta_z^2}(\tilde{\phi}_{i,j+1} + \tilde{\phi}_{i,j-1}) \right) / \Delta$$

$$\Delta = \left(\frac{1}{\delta_x^2} + \frac{1}{\delta_z^2} \right)$$

Two-grid iteration $I_2(\nu_1, \nu_2)$

$$\tilde{\phi}^h \leftarrow S_{\nu_1}\tilde{\phi}^h, \quad r^h = f^h - L^h\tilde{\phi}^h, \quad r^H = I_h^H r^h$$
$$e^H = (L^H)^{-1} r^H, \quad e^h = I_H^h e^H$$
$$\tilde{\phi}^h \leftarrow \tilde{\phi}^h + e^h, \quad \tilde{\phi}^h \leftarrow S_{\nu_2}\tilde{\phi}^h$$

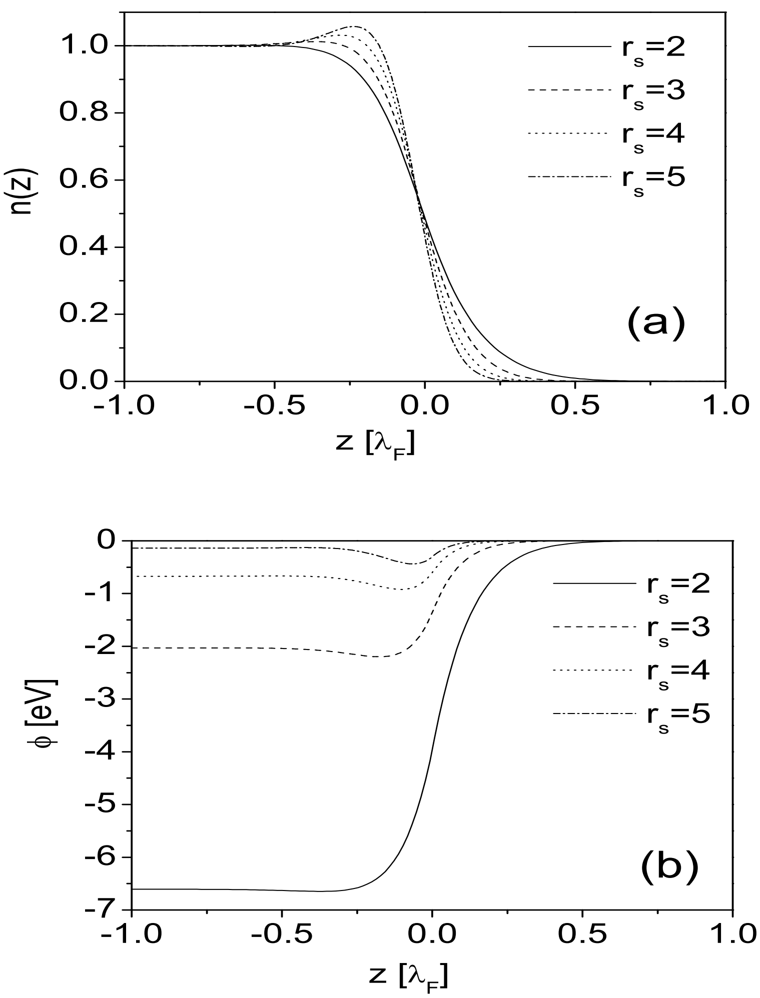
Recursive two-grid iteration $\mathcal{R}I_2$ on N_l coarser grids $\Omega^{2h}, \Omega^{4h}, \ldots$

$$l = 2, \ldots, N_l \quad n = 1, \ldots, N_v, \quad H = 2lh, 2(l-1)h, \ldots h,$$

$$\phi^h \leftarrow \mathcal{R}I_2\tilde{\phi}^h$$

Numerical results for $N_v = 15, \nu_1 = \nu_2 = 5$. ($\delta_x = 0.11, \delta_z = 0.08$).

Numerical results for flat surfaces.



Metallic work functions

r_s	present result	(A)	(B)
2	3.70	3.70	3.89
3	3.22	3.22	3.50
4	2.83	2.84	3.06
5	2.53	2.55	2.73

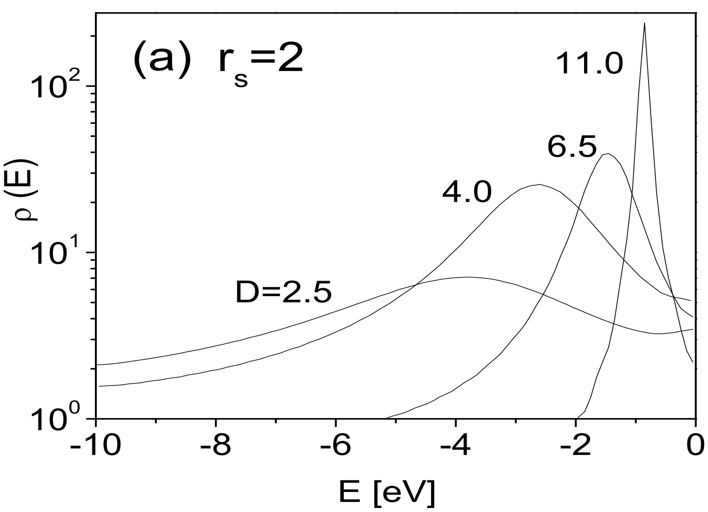
Work functions W in eV for flat jellium surfaces, compared with calculations (A) and (B).

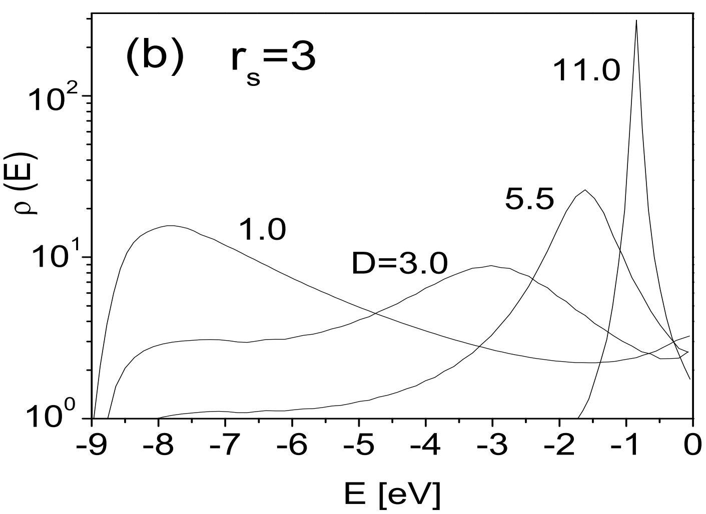
(A) A. Chizmeshya and E. Zaremba, Phys. Rev. B **37**, 2805 (1988).

(B) N. D. Lang and W. Kohn, Phys. Rev. B**1**, 4555 (1970).

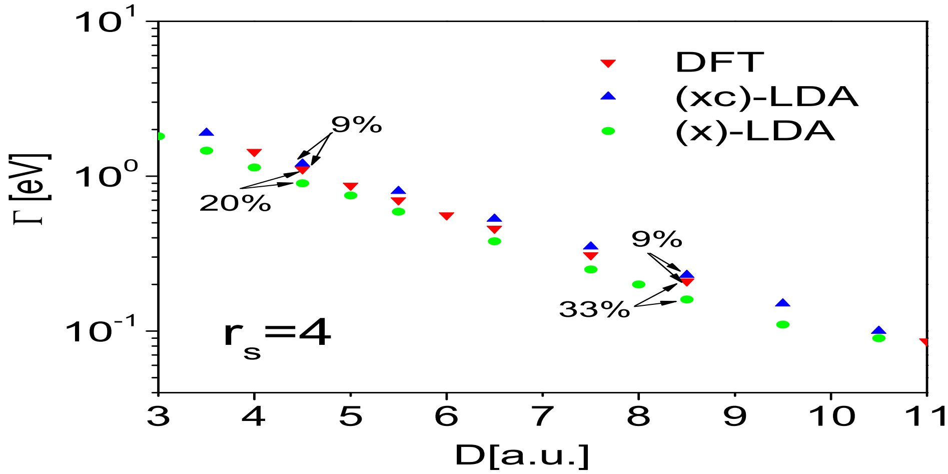
$$W = -\mu = -(\frac{5}{3}(\psi_{\rm bulk})^{4/3} + v_{\rm xc}(\psi_{\rm bulk}) + \phi_{\rm bulk})$$

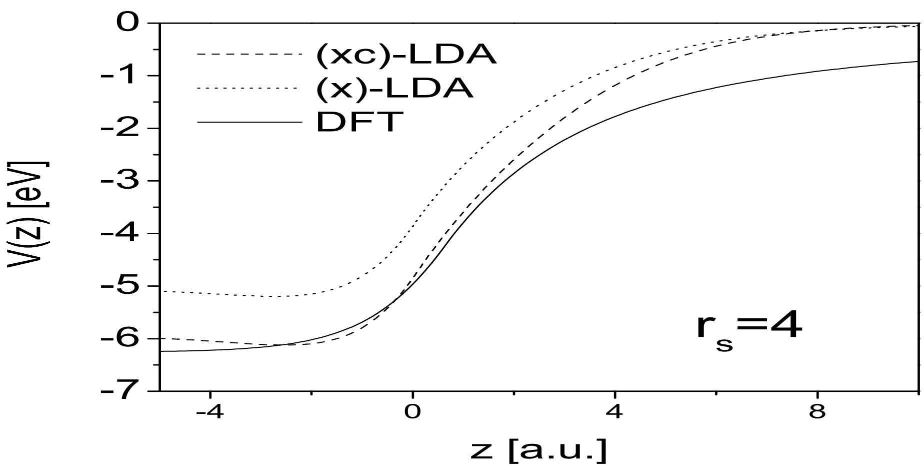
Projected density of states (Al and Cu surfaces)

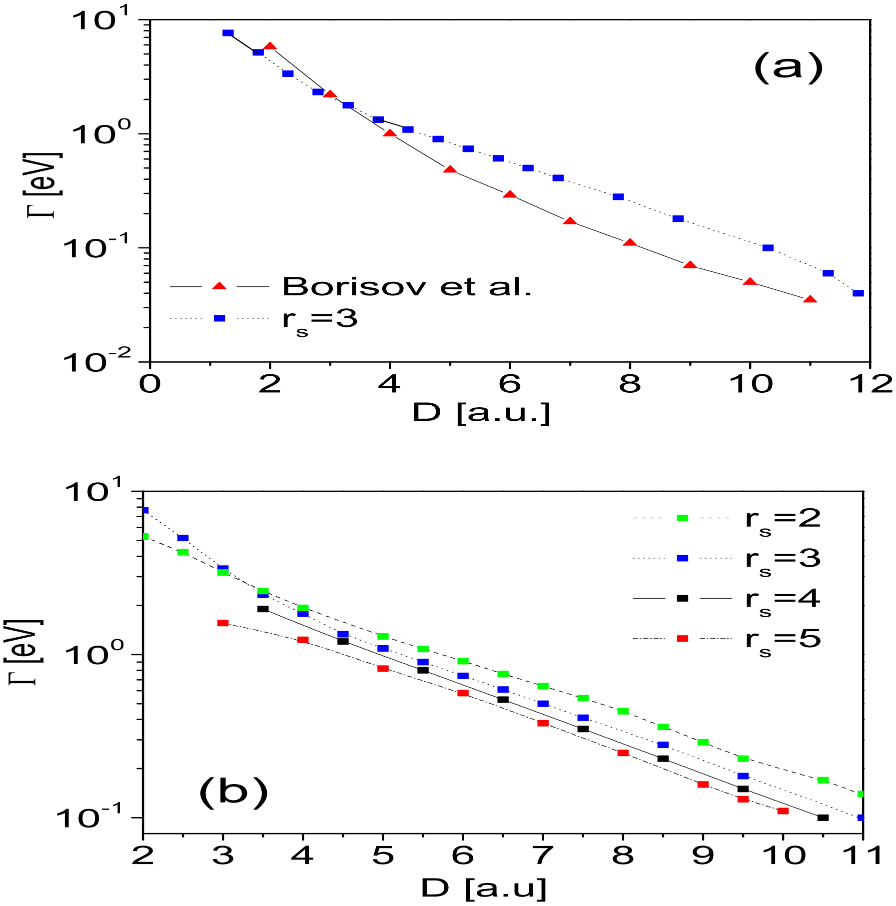




Static widths.

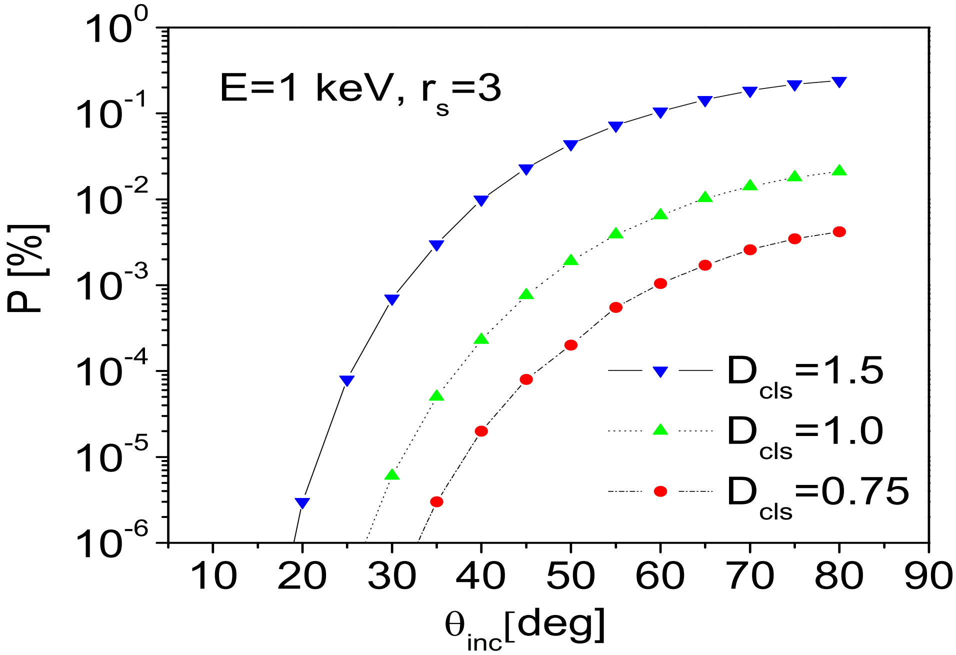


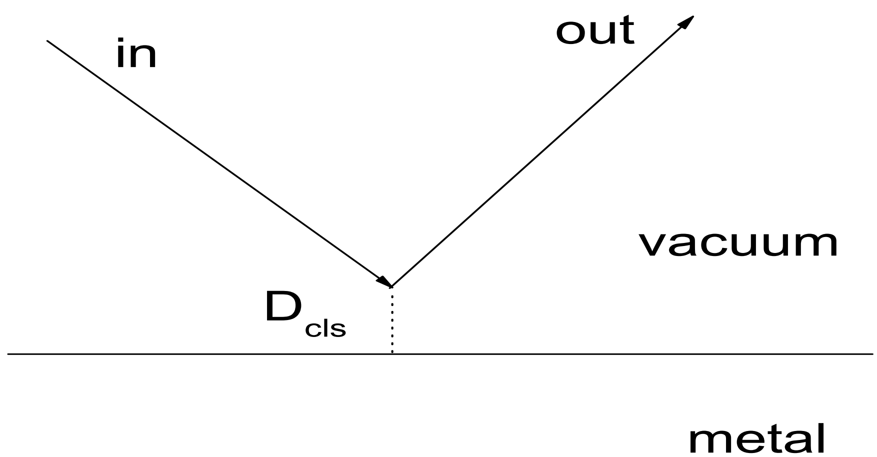




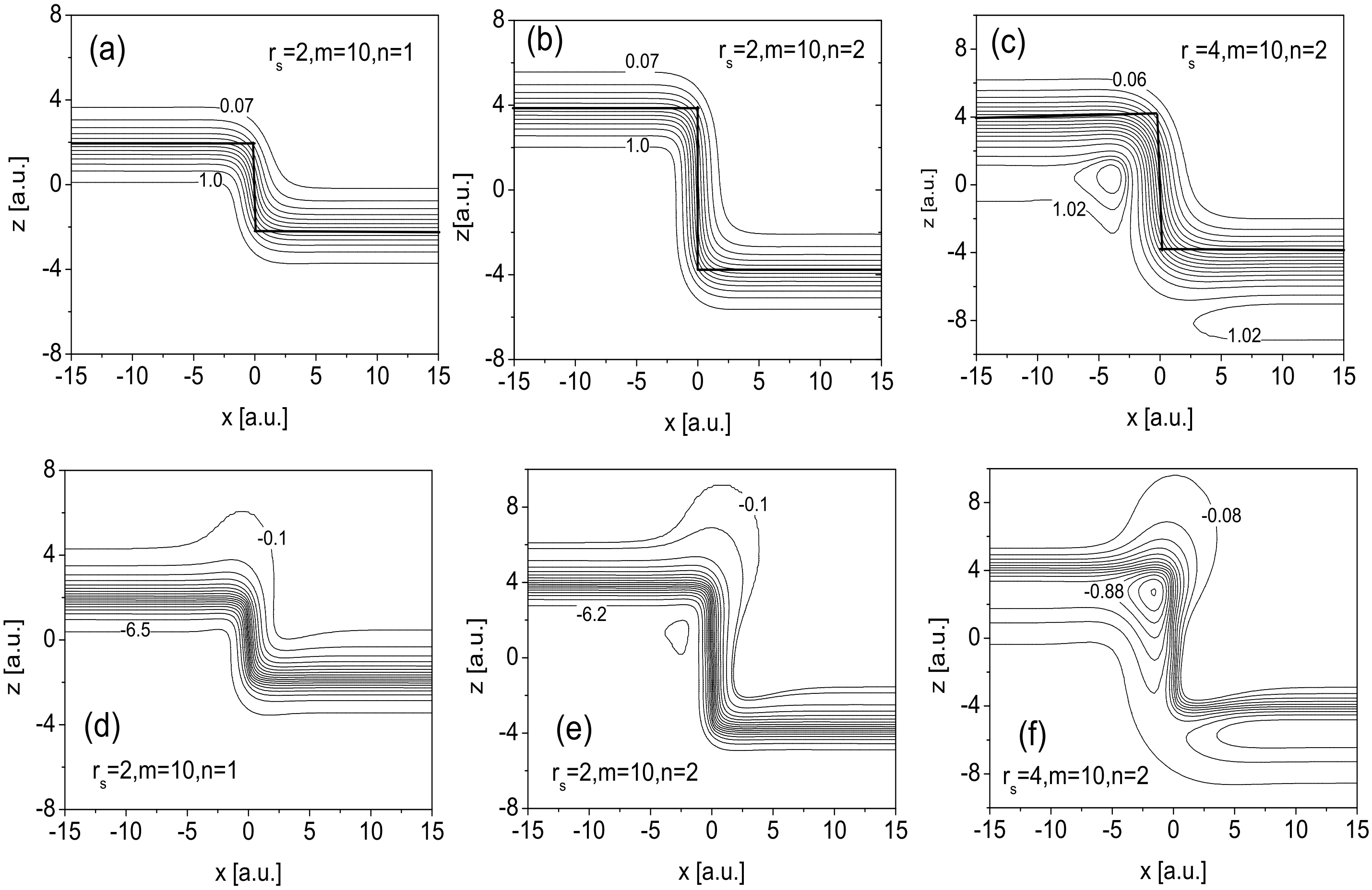
(a)
Borisov et al.
$r_s=3$
Γ [eV]
D [a.u.]
(b)
$r_s=2$
$r_s=3$
$r_s=4$
$r_s=5$
Γ [eV]
D [a.u]

Ion-survival probability near flat Cu surafce





Numerical results for vicinal surfaces



Work functions for vicinal metallic surfaces

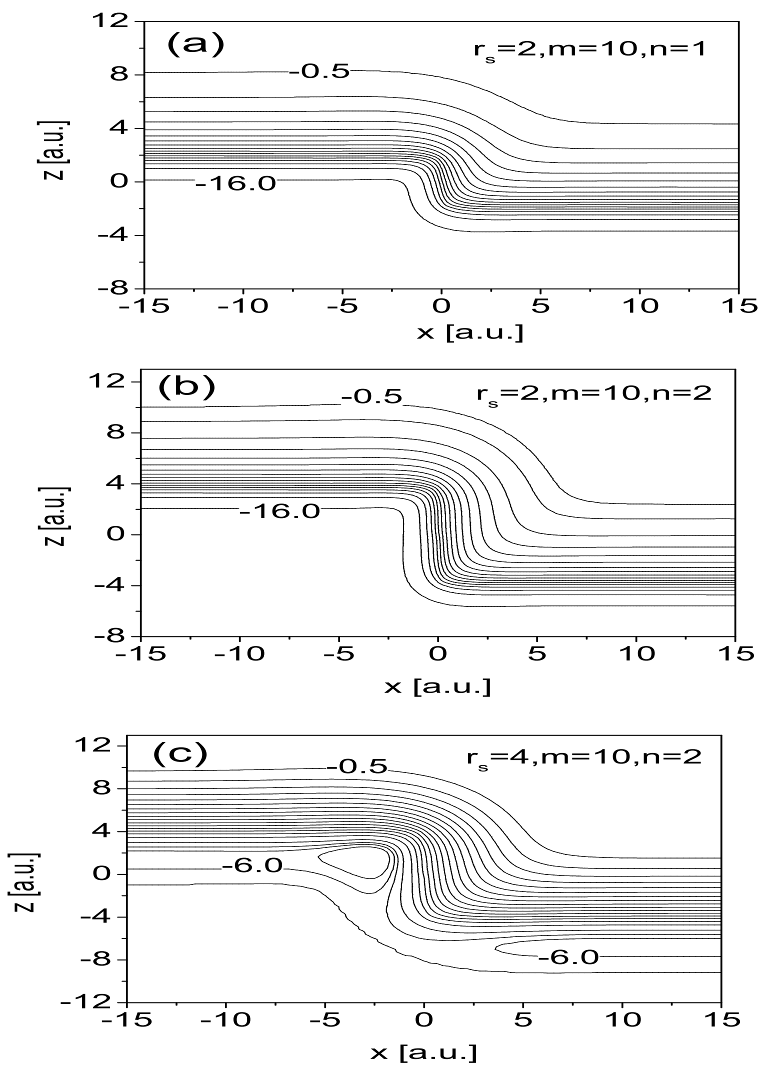
			this work		literature data
r_s	m	n	W	ΔW	$\Delta W[Ref.]$
2	10	1	3.66	0.03	0.03 (A)
2	10	2	3.63	0.07	0.05 (A)
2.7	8	1	3.30	0.05	0.03 (B) for Cu(117)
					0.04 (B) for Cu(119)
2.7	8	2	3.26	0.09	
3	10	2	3.16	0.06	
4	10	2	2.75	0.08	

Work function W and work function change ΔW in eV compared with results based on the Kohn-Sham equations (A) and experimental data for vicinal Cu(117) and Cu(119) surfaces (B).

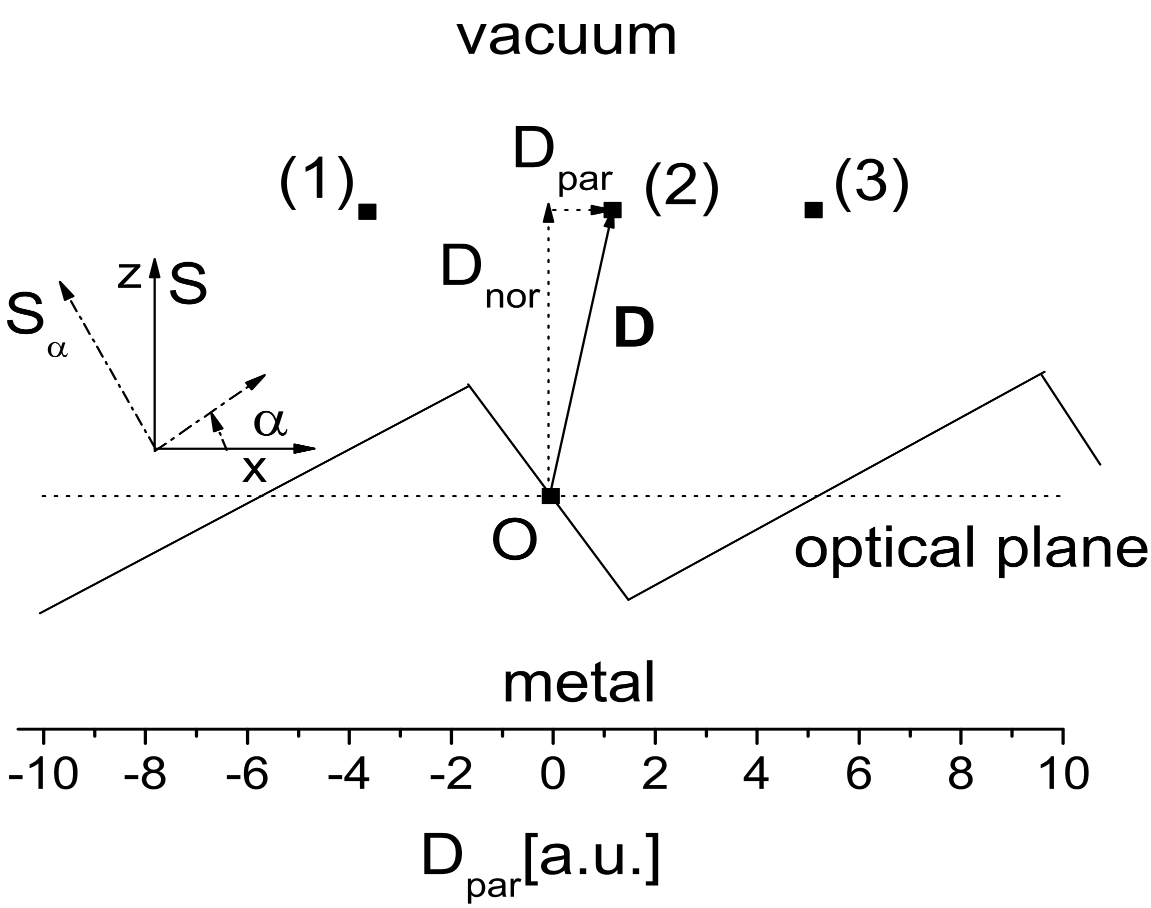
(A) H. Ishida and A. Liebsch, Phys. Rev. B **46**, 7153 (1992).

(B) M. Roth, M. Pickel, J. Wang, M. Weinelt, Th. Fauster, Appl. Phys. B **74**, 661 (2002).

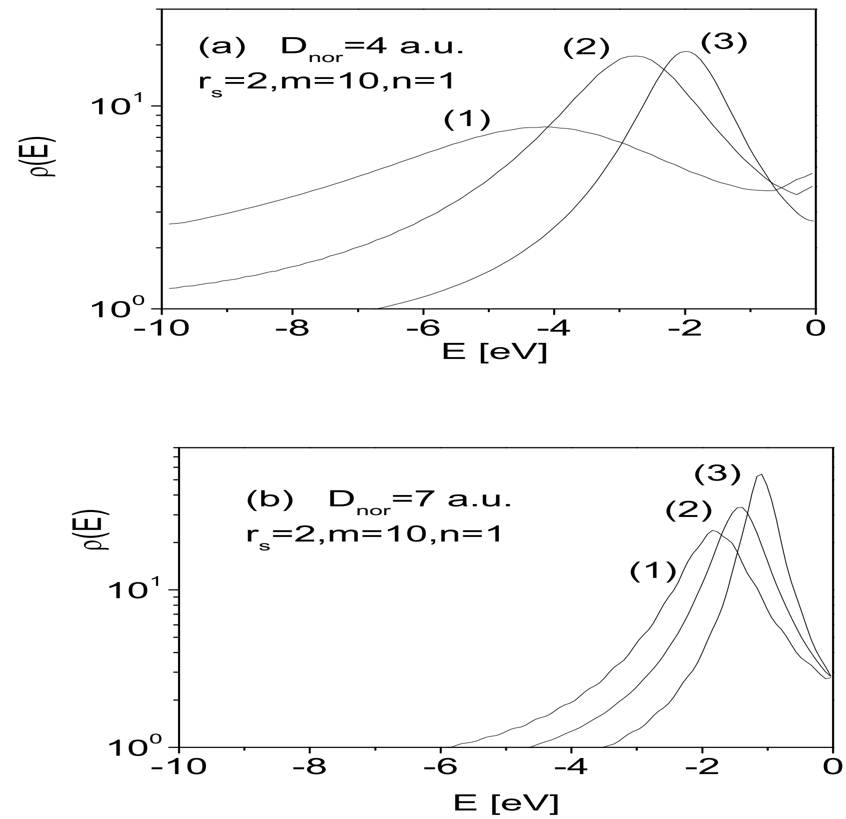
Surface potentials for Al and Na



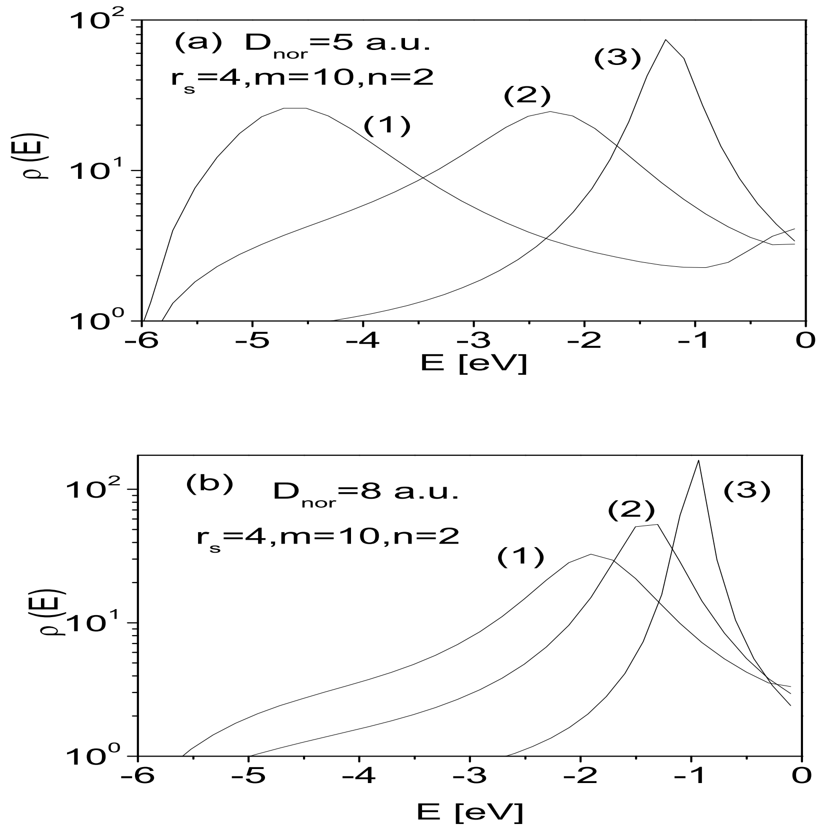
Projected density of states (PDOS)

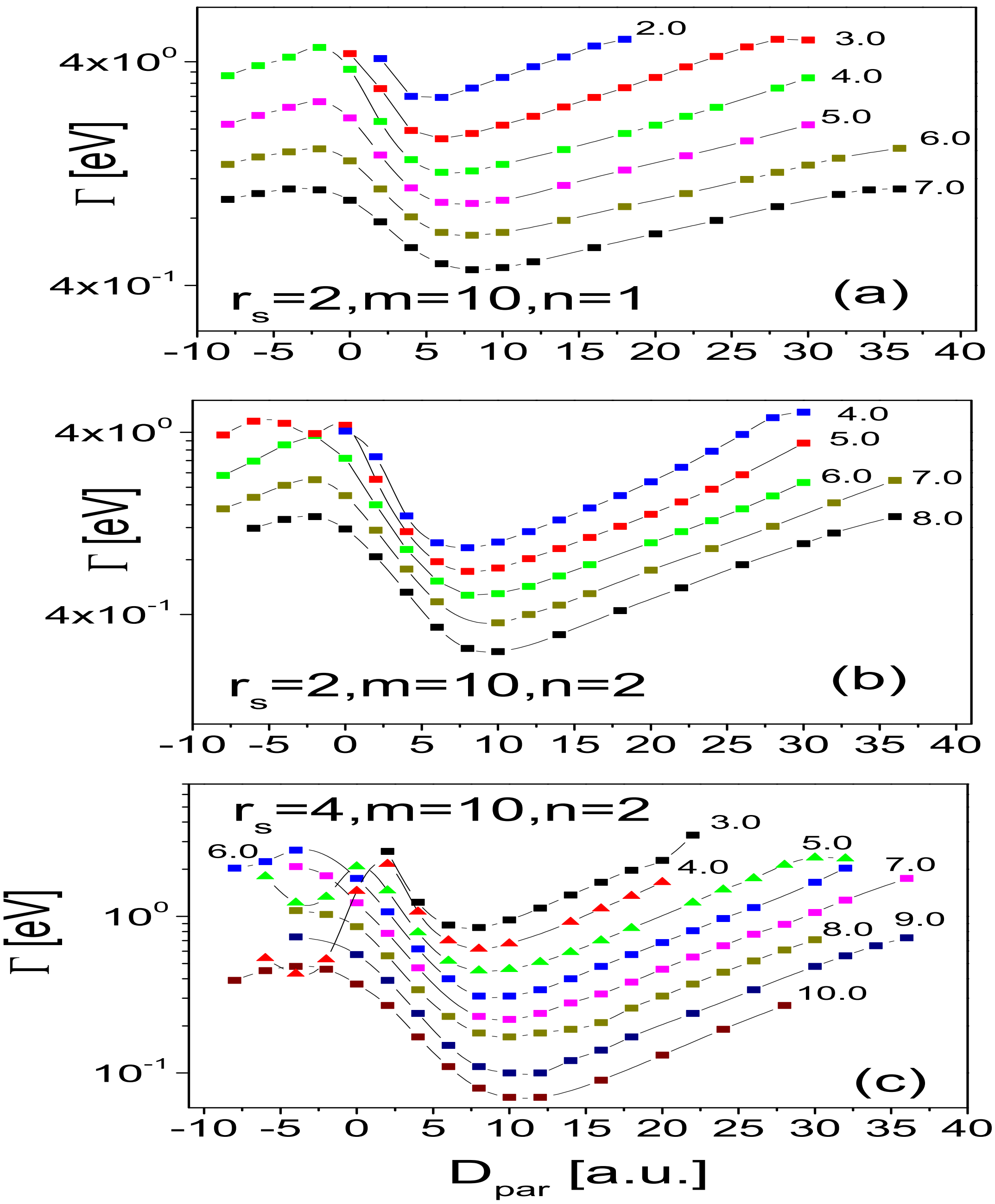


PDOS, vicinal Al surface, $(m, n) = (10, 1)$



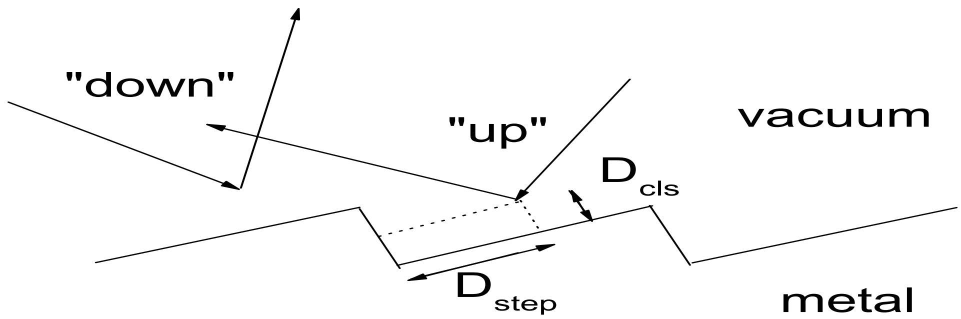
PDOS, vicinal Na surface, $(m, n) = (10, 2)$

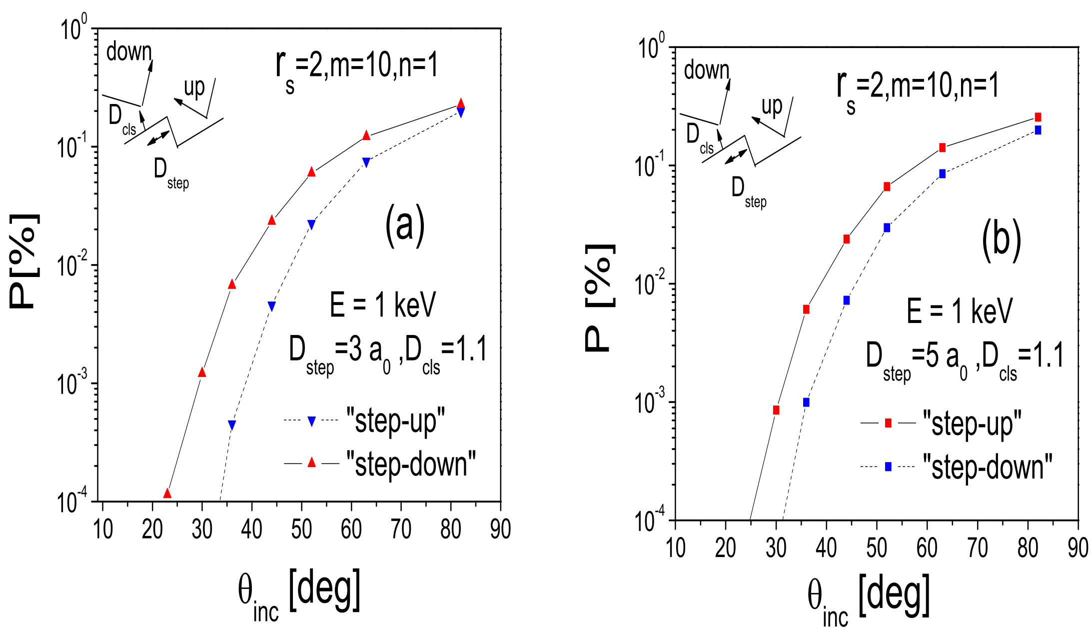


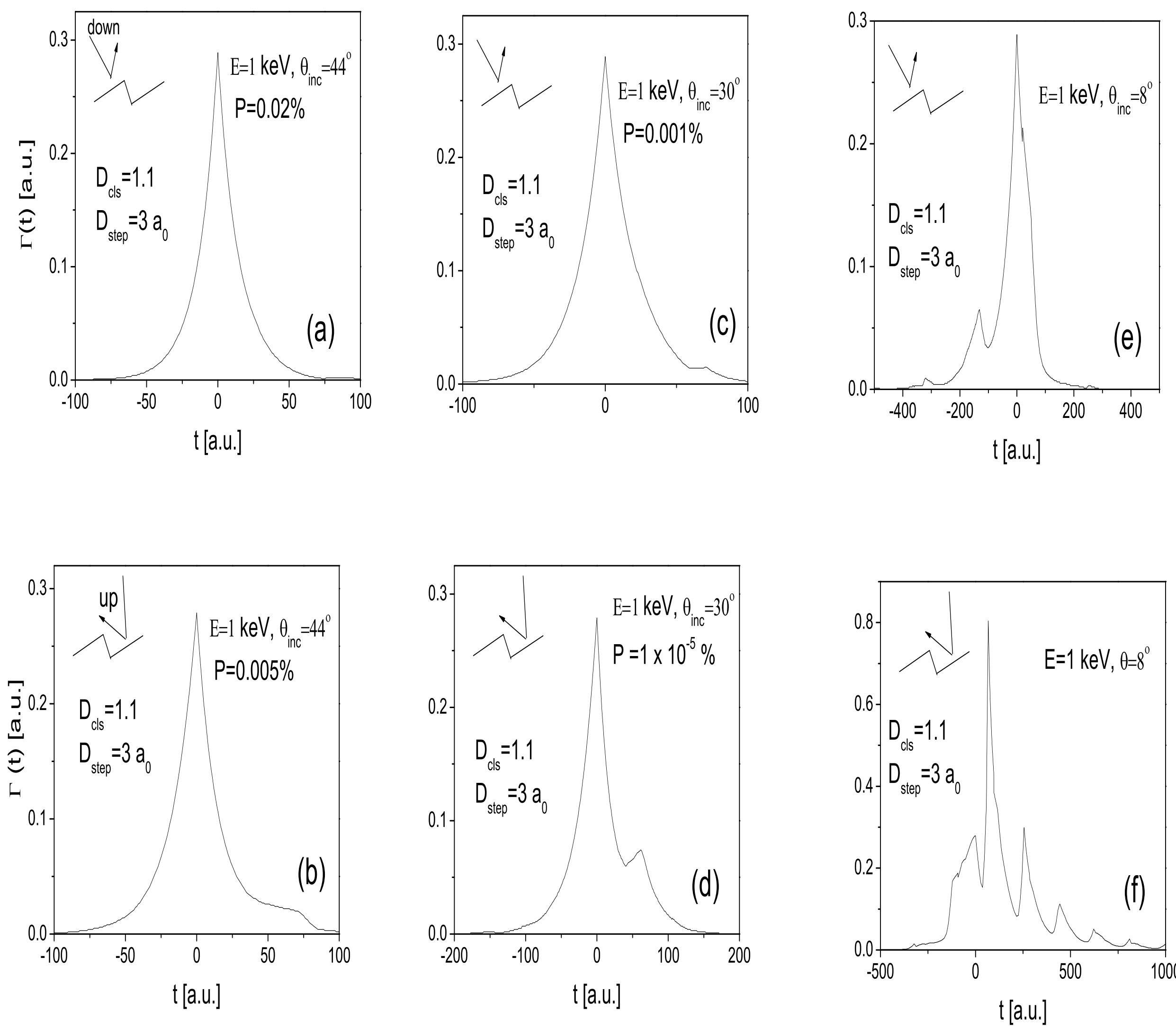


Γ [eV]
4x10⁰
4x10⁻¹
2.0
3.0
4.0
5.0
6.0
7.0
r_s=2,m=10,n=1
(a)
-10 -5 0 5 10 15 20 25 30 35 40
Γ [eV]
4x10⁰
4x10⁻¹
4.0
5.0
6.0
7.0
8.0
r_s=2,m=10,n=2
(b)
-10 -5 0 5 10 15 20 25 30 35 40
r_s=4,m=10,n=2
Γ [eV]
10⁰
10⁻¹
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
(c)
-10 -5 0 5 10 15 20 25 30 35 40
D_par [a.u.]

Ion-survival probability near vicinal Al surface, $(m, n) = (10, 1)$







down
E=1 keV, θ_{inc}=44°
P=0.02%
D_{cls}=1.1
D_{step}=3 a_0
(a)
Γ(t) [a.u.]
t [a.u.]
E=1 keV, θ_{inc}=30°
P=0.001%
D_{cls}=1.1
D_{step}=3 a_0
(c)
E=1 keV, θ_{inc}=8°
D_{cls}=1.1
D_{step}=3 a_0
(e)
t [a.u.]
up
E=1 keV, θ_{inc}=44°
P=0.005%
D_{cls}=1.1
D_{step}=3 a_0
(b)
Γ (t) [a.u.]
t [a.u.]
E=1 keV, θ_{inc}=30°
P =1 x 10^{-5} %
D_{cls}=1.1
D_{step}=3 a_0
(d)
t [a.u.]
E=1 keV, θ=8°
D_{cls}=1.1
D_{step}=3 a_0
(f)
t [a.u.]

Free-electron gas in a volume Ω at $T = 0^\circ$ K

$$H = K$$

$$K = \sum_{\mathbf{k},\sigma} \frac{k^2}{2} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}, \qquad \{c_{\mathbf{k},\sigma}, c^\dagger_{\mathbf{k}',\sigma'}\} = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\sigma,\sigma'}$$

$$|0\rangle = \mathcal{A}\left(\prod_i |\mathbf{k}_i, \sigma_i\rangle\right), \quad |\mathbf{k}_i| < k_F, \quad \phi_{\mathbf{k},\sigma}(\mathbf{r}, \lambda) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} \delta_{\sigma\lambda}$$

$$n_{\mathbf{k},\sigma} = \langle c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k}\sigma}\rangle_0 = \theta(k_F - k)$$

$$E_0 = \langle K\rangle_0 = 2\sum_{\mathbf{k}} \theta(k_F - k)\frac{k^2}{2} = 2\Omega \int_{k<k_F} \frac{d^3\mathbf{k}}{(2\pi)^3}\frac{k^2}{2} = \frac{\Omega k_F^5}{10\pi^2}$$

$$N = 2\sum_{\mathbf{k}} \theta(k_F - k) = \Omega \frac{k_F^3}{3\pi^2} \Rightarrow n = \frac{N}{\Omega} = \frac{3}{4\pi r_s^3} = \frac{k_F^3}{3\pi^2}$$

$$t(n) = E_0/N = \frac{3}{10}k_F^2 = \frac{3}{10}(3\pi^2)^{2/3} n^{2/3}$$

Interacting electron gas in jellium model

$$H = K + V$$

$$V = \frac{1}{2\Omega}\sum_{\mathbf{k},\sigma}\sum_{\mathbf{k}',\sigma'}\sum_{\mathbf{q}\neq 0}\frac{4\pi}{q^2}c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c^\dagger_{\mathbf{k}'-\mathbf{q},\sigma'}c_{\mathbf{k}',\sigma'}c_{\mathbf{k},\sigma}$$

Ground state energy in Hartree-Fock approximation $E = E_0 + \delta E^{(1)}$

$$\delta E^{(1)} = \frac{1}{2\Omega}\sum_{\mathbf{k},\sigma}\sum_{\mathbf{k}',\sigma'}\sum_{\mathbf{q}\neq 0}\frac{4\pi}{q^2}\langle 0|c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c^\dagger_{\mathbf{k}'-\mathbf{q},\sigma'}c_{\mathbf{k}',\sigma'}c_{\mathbf{k},\sigma}|0\rangle$$

$$\langle 0|c^\dagger_{\mathbf{k}+\mathbf{q},\sigma}c^\dagger_{\mathbf{k}'-\mathbf{q},\sigma'}c_{\mathbf{k}',\sigma'}c_{\mathbf{k},\sigma}|0\rangle = \delta_{\mathbf{q},0}n_{\mathbf{k},\sigma}n_{\mathbf{k}',\sigma'} - \delta_{\mathbf{k}+\mathbf{q}-\mathbf{k}'}n_{\mathbf{k},\sigma}n_{\mathbf{k}',\sigma'}$$

$$\Rightarrow \delta E^{(1)} = -\frac{1}{2\Omega}\sum_{\mathbf{k},\sigma}\sum_{\mathbf{k}',\sigma'}\sum_{\mathbf{q}}\frac{4\pi}{q^2}\delta(\mathbf{k}+\mathbf{q}-\mathbf{k}')\delta_{\sigma,\sigma'}n_{\mathbf{k},\sigma}n_{\mathbf{k}'\sigma'} =$$

$$= -\frac{1}{2\Omega}\sum_{\mathbf{q},\mathbf{k},\sigma}\frac{4\pi}{q^2}\theta(k_F-k)\theta(k_F-|\mathbf{k}-\mathbf{q}|) = -\frac{2\Omega}{(2\pi)^3}k_F^4 \Rightarrow$$

$$\varepsilon_x(n) = \delta E^{(1)}/N = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}n^{1/3}$$

Structure factor

$$S(\mathbf{q}) = \frac{1}{n^2}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\theta(k_F-k)\theta(k_F-|\mathbf{k}-\mathbf{q}|), \quad \mathbf{q}\neq 0$$

$$P(\mathbf{r}) = \frac{4\pi r^2}{\Omega}\left\{1-\left[\frac{3}{k_F^3r^3}\left(\sin(k_Fr)-k_Fr\cos(k_Fr)\right)\right]^2\right\}$$

Correlation energy, RPA.

$$H = H_0 + V, \qquad H_0 = K$$

$$E_{\rm corr} = \sum_{k=2}^{\infty} \delta E^{(k)} = \left\langle V \frac{1}{E_0 - K} V \right\rangle_0 + \left\langle V \frac{1}{E_0 - K} V \frac{1}{E_0 - K} V \right\rangle_0 + \dots$$

$$\delta E^{(2)} = \delta E^{(2)}_x + \delta E^{(2)}_c$$

$$\delta E^{(2)}_x = \text{const} \times N \int d^3\mathbf{q} \int d^3\mathbf{k} \int d^3\mathbf{p} \frac{n_\mathbf{k} n_\mathbf{p}(1 - n_{\mathbf{p}+\mathbf{q}})(1 - n_{\mathbf{k}+\mathbf{q}})}{q^2(\mathbf{q}+\mathbf{k}+\mathbf{p})^2(q^2 + \mathbf{q}\cdot(\mathbf{k}+\mathbf{p}))}$$

$$\delta E^{(2)}_c = \text{const} \times N \int d^3\mathbf{q} \int d^3\mathbf{k} \int d^3\mathbf{p} \frac{n_\mathbf{k} n_\mathbf{p}(1 - n_{\mathbf{p}+\mathbf{q}})(1 - n_{\mathbf{k}+\mathbf{q}})}{q^4(q^2 + \mathbf{q}\cdot(\mathbf{k}+\mathbf{p}))}$$

$$\int d^3\mathbf{k} \int d^3\mathbf{p} \frac{1}{q^4(q^2 + \mathbf{q}\cdot(\mathbf{k}+\mathbf{p}))} \sim q, \quad q \to 0, \quad \delta E^{(2)}_c \sim \int \frac{dq}{q}$$

Gell-mann-Brueckner series, high density limit $r_s \to 0$

$$\delta E = \sum_k \int \frac{d^3\mathbf{q}}{(2\pi)^3} \left(\frac{2\pi}{\Omega q^2}\right)^k A_k(q)(-1)^k,$$

$$A_k(q) = \frac{1}{k} \int dt_1 \dots \int dt_k F_q(t_1) \dots F_q(t_k) \delta(t_1 + + \dots + t_k),$$

$$F_q(t) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-|t|(q^2/2 + \mathbf{q}\cdot\mathbf{k})} \theta(k_F - k)\theta(|\mathbf{k}+\mathbf{q}| - k_F),$$

$$\Rightarrow \varepsilon_c(n) = \delta E_c/N = \frac{1}{2}(\underbrace{0.0622 \ln r_s}_{E_{s.r.}} - \underbrace{0.094}_{E_{l.r.}}) + O(r_s \ln r_s), \Rightarrow$$

Screening of the Coulomb interactions, polarization propagator

$$\Pi(\mathbf{q},\omega) = \frac{1}{2}(\tilde{F}_+(q, i\omega + 0) - \tilde{F}_-(q, i\omega - 0))$$

$$u_{\text{eff}}(\mathbf{q},\omega) = \frac{4\pi}{q^2} + \frac{4\pi}{q^2}\Pi(\mathbf{q},\omega)\frac{4\pi}{q^2} + \ldots = \frac{4\pi/q^2}{1 - \Pi(\mathbf{q},\omega)4\pi/q^2}$$

In static limit $\omega \to 0$,

$$\Pi(\mathbf{q},0) = \frac{k_F}{2\pi^2}\left\{-1 + \frac{k_F}{q}\left(1 - \frac{1}{4}\frac{q^2}{k_F^2}\right)\ln\left|\frac{1 - q/2k_F}{1 + q/2k_F}\right|\right\}$$

and if $q \ll k_F$, $\Pi \approx -k_F/2\pi^2 \Rightarrow$

$$u_{\text{eff}}(\mathbf{q}) = \frac{4\pi}{q^2 + 2k_F/\pi}, \quad q_{\text{TF}} = \sqrt{2k_F/\pi}$$

Low-density limit, $r_s \to \infty$, $H = K + V$, $K \approx 0$

$$\varepsilon_c(n) = E_c/N \approx \frac{1}{2}\left(\frac{3}{5r_s} - \frac{3}{2r_s}\right) = -\frac{0.44}{r_s}, \quad \Rightarrow$$

Wigner interpolation formula

$$\varepsilon_c(n) = -\frac{0.44}{7.8 + r_s}$$