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ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11-15 September 2000

Miramare - Trieste, Italy

Lifetimes of electrons near the Fermi level

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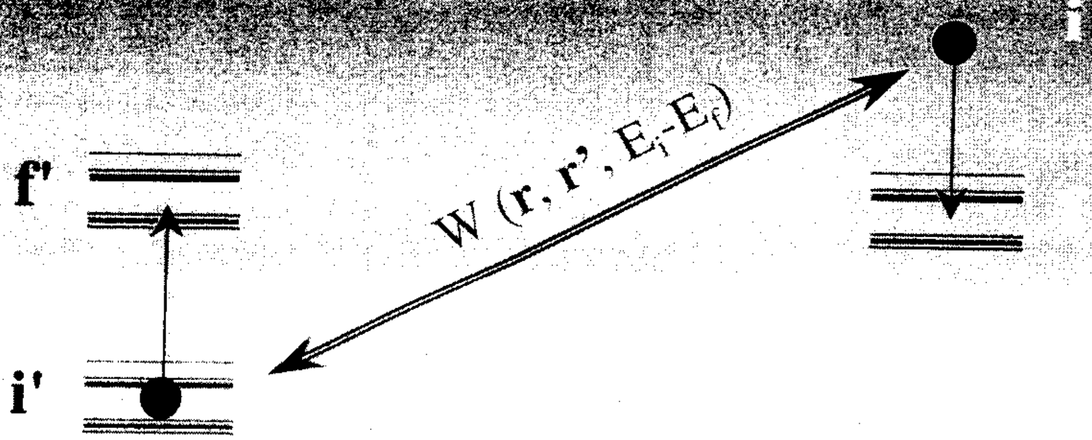

Lifetimes of electrons near the Fermi level

Adriatic School
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Universidad del País Vasco
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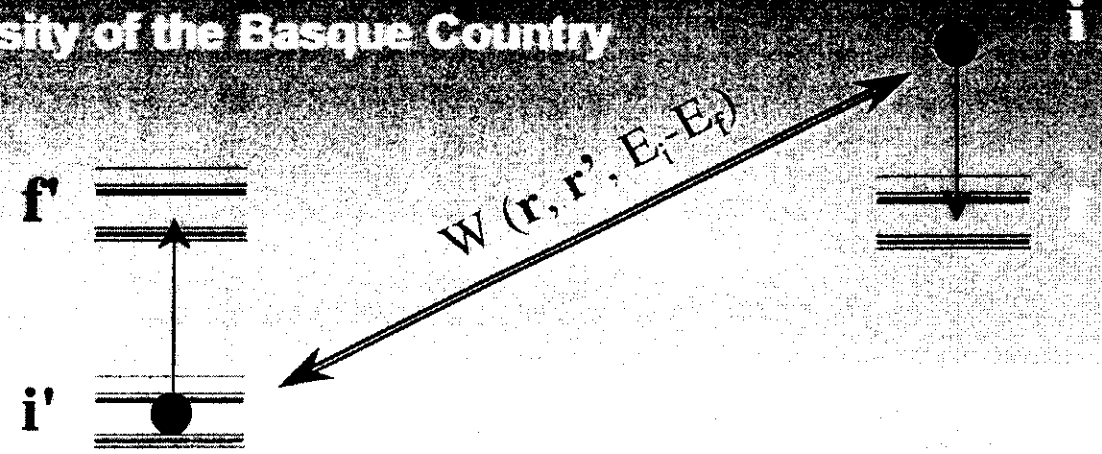
D.I.P.C.



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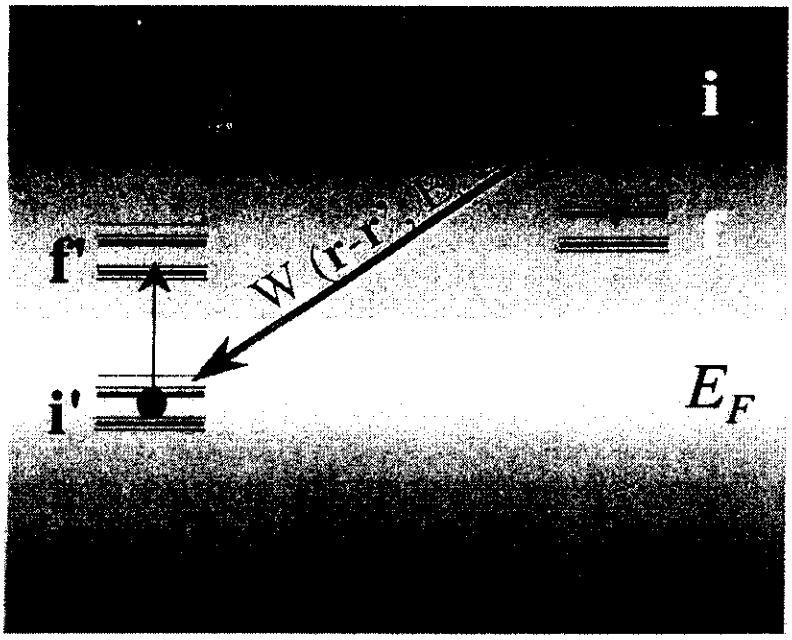
DOS approach



Random-k approximation

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}\int_{E_F}^{E} dE\ \rho(E')\int_0^{E_F} d\varepsilon\rho(\varepsilon)\rho(\varepsilon+\omega)\,|\,\mathrm{M}\,(\omega)\,|^2$$

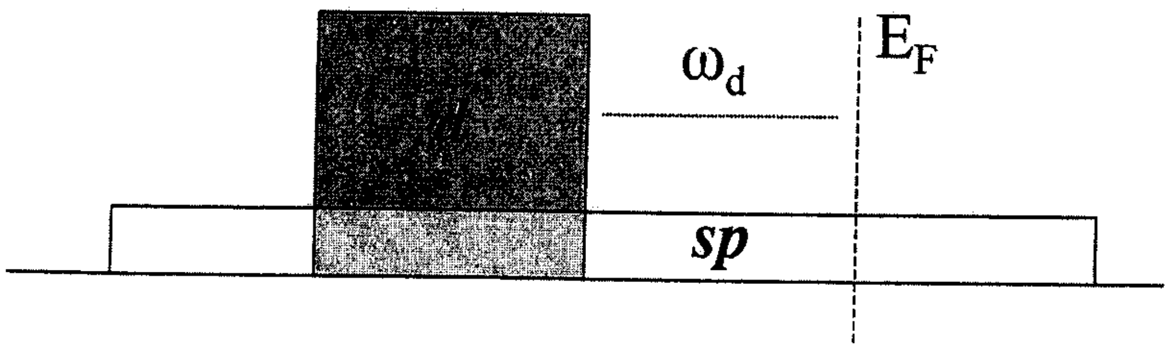
(ω = E -E')

Constant matrix elements $|\,\mathrm{M}\,(\omega)\,|^2 = |\mathrm{M}\,|^2$ but dependent on the character of the bands

$$\mathrm{M} = \mathrm{M}_{f\ f'}^{i\ i'}$$

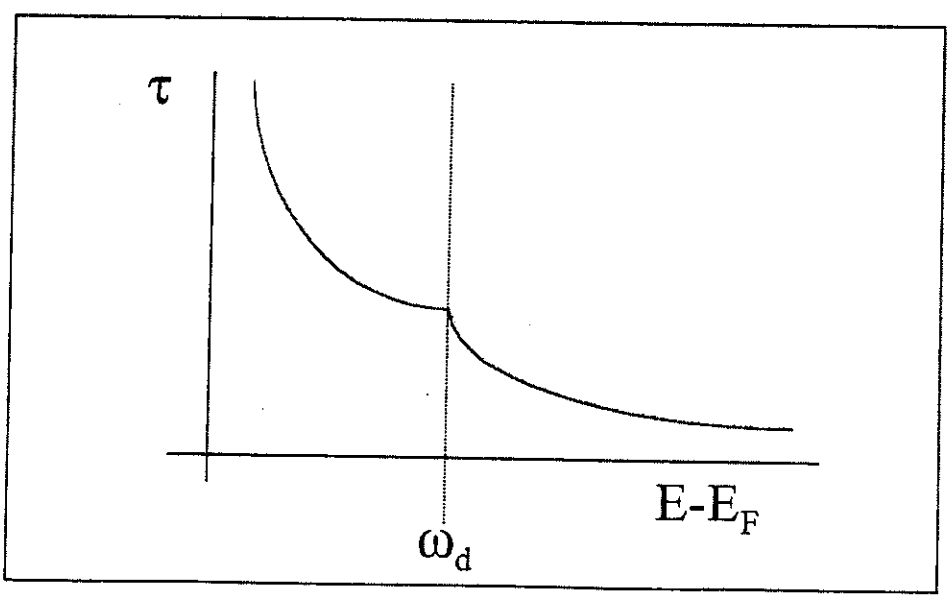
DOS approach: Noble metals

- **Simple description**



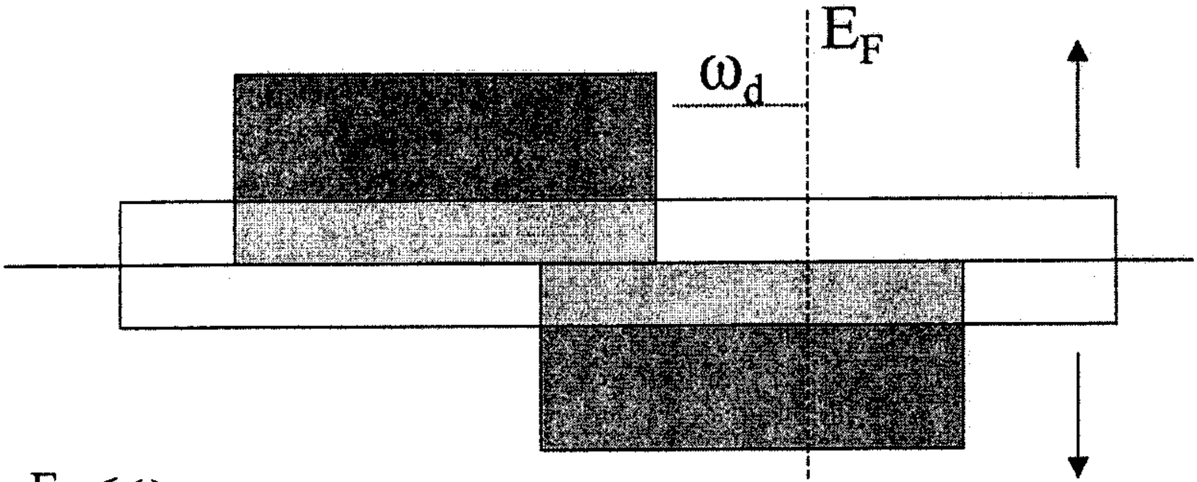
$$\tau^{-1} = M_{ss}^{ss} \, (E - E_F)^2 \qquad (E - E_F < \omega_d)$$

$$\tau^{-1} = M_{ss}^{ss} \, (E - E_F)^2$$
$$+ \, M_{ss}^{sd} \, (E - E_F - \omega_d)^2 \qquad (E - E_F > \omega_d)$$



DOS approach: Cobalt

- **Simple description**



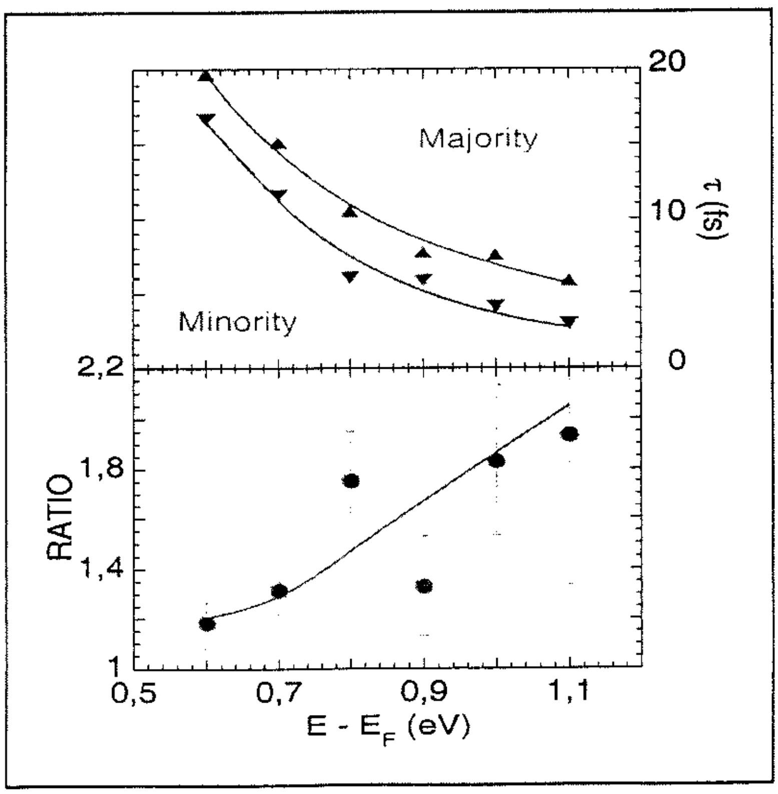
•$E - E_F < \omega_d$

$$\tau^{\uparrow}/\tau_{\downarrow} = \frac{c^{\downarrow}_0 \; (E - E_F)^2}{c^{\uparrow}_0 \; (E - E_F)^2}$$

•$E - E_F > \omega_d$

$$\tau^{\uparrow}/\tau_{\downarrow} = \frac{c^{\downarrow}_0 \; (E - E_F)^2 + c^{\downarrow}_1 (E - E_F - \omega_d)^2}{c^{\uparrow}_0 \; (E - E_F)^2 + c^{\uparrow}_1 (E - E_F - \omega_d)^2} = f(E)$$

Zarate *et al.*
Exp. M. Aeschlimann *et al.*



DOS vs. SCREENING

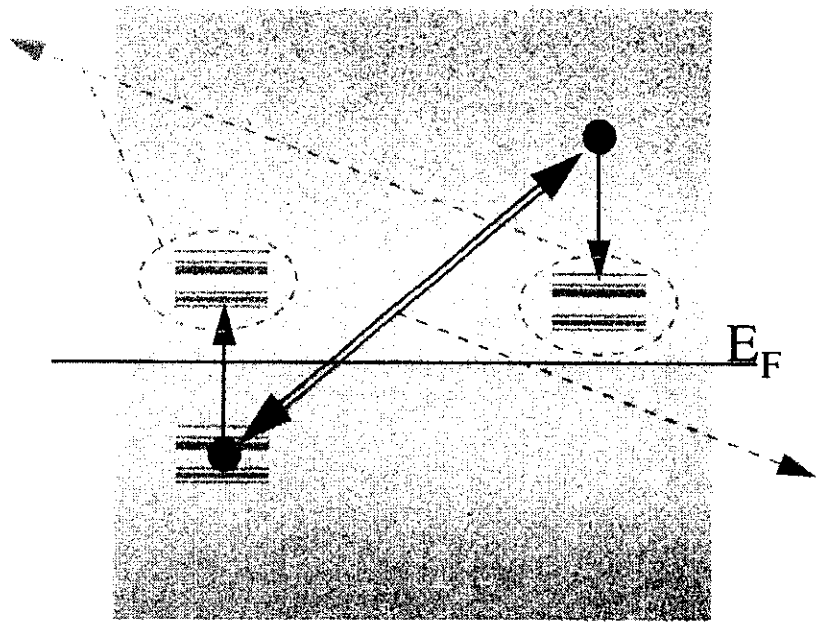
Density of states

More DOS

More phase space available

More probability for the process

Shorter lifetimes



Screening

More DOS

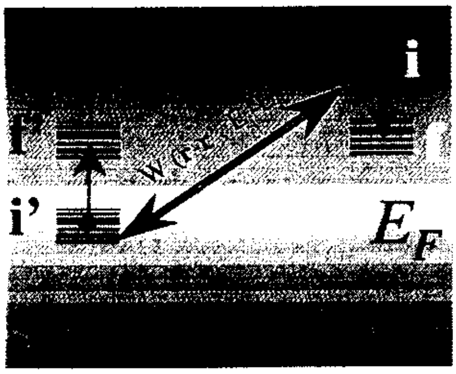
More screening

Weaker interaction

Longer lifetimes

Free electrons
Quinn (1962)

$$\tau^{-1} = \frac{\sqrt{3}\,\pi^2}{128}\,\frac{\omega_p}{E_F^2}\,(E - E_F)^2 \longrightarrow \tau \approx \frac{263\, r_s^{-5/2}}{(E - E_F)^2}$$



- **LIFETIME**

$$\tau^{-1} = -2\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\phi_i^*(\mathbf{r})\mathrm{Im}\Sigma(\mathbf{r},\mathbf{r}',\mathbf{k}_{\|};\epsilon_i)\phi_i(\mathbf{r}')$$

- **LIFETIME-SCREENED INTERACTION**

$$\begin{aligned}\tau^{-1} &= -2\sum_f{}' \int \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\phi_i^*(\mathbf{r})\phi_f^*(\mathbf{r}') \\ &\times \mathrm{Im}W(\mathbf{r},\mathbf{r}';\omega)\phi_i(\mathbf{r}')\phi_f(\mathbf{r})\end{aligned}$$

- **SELF-ENERGY**

$$\begin{aligned}\mathrm{Im}\Sigma(\mathbf{r},\mathbf{r}';\epsilon_i > E_F) &= \sum_{E_F\le\epsilon_f\le\epsilon_i} \phi_f^*(\mathbf{r}') \\ &\times \mathrm{Im}W(\mathbf{r},\mathbf{r}';\epsilon_i-\epsilon_f)\phi_f(\mathbf{r})\end{aligned}$$

LINEAR RESPONSE

- SCREENED INTERACTION

$$W(\mathbf{r},\mathbf{r}';\omega) = v(\mathbf{r}-\mathbf{r}') + \int d\mathbf{r}_1 d\mathbf{r}_2 \;\; v(\mathbf{r}_2-\mathbf{r}')$$
$$\times \left[v(\mathbf{r}-\mathbf{r}_1) + K^{xc}(\mathbf{r},\mathbf{r}_1;\omega)\right] \quad \chi(\mathbf{r}_1,\mathbf{r}_2;\omega)$$

- DENSITY RESPONSE FUNCTION

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \chi^0(\mathbf{r},\mathbf{r}';\omega) + \int d\mathbf{r}_1 d\mathbf{r}_2 \;\; \chi^0(\mathbf{r},\mathbf{r}_1;\omega)$$
$$\times \left[v(\mathbf{r}_1-\mathbf{r}_2) + K^{xc}(\mathbf{r}_1,\mathbf{r}_2;\omega)\right] \quad \chi(\mathbf{r}_2,\mathbf{r}';\omega)$$

- DENSITY RESPONSE FUNCTION OF NON-INTERACTING GAS

$$\chi^0(\mathbf{r},\mathbf{r}';\omega) = \; 2 \; \sum_{i,j} \frac{\theta(E_F-\omega_i) - \theta(E_F-\omega_j)}{\epsilon_i - \epsilon_j + (\omega + i\eta)}$$
$$\times \quad \phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_j(\mathbf{r}')\phi_i^*(\mathbf{r}')$$

PERIODIC CRYSTALS

- LIFETIME

$$\tau^{-1} = \frac{1}{\pi^2}\sum_f{}' \int_{\mathrm{BZ}} \mathrm{d}\mathbf{q} \sum_{\mathbf{G}} \sum_{\mathbf{G}'} \frac{B^*_{if}(\mathbf{q}+\mathbf{G}) B_{if}(\mathbf{q}+\mathbf{G}'}{|\mathbf{q}+\mathbf{G}|^2}$$
$$\times \ \mathrm{Im}\left[-\epsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\varepsilon_{\mathbf{k},i}-\varepsilon_{\mathbf{k}-\mathbf{q},f})\right]$$

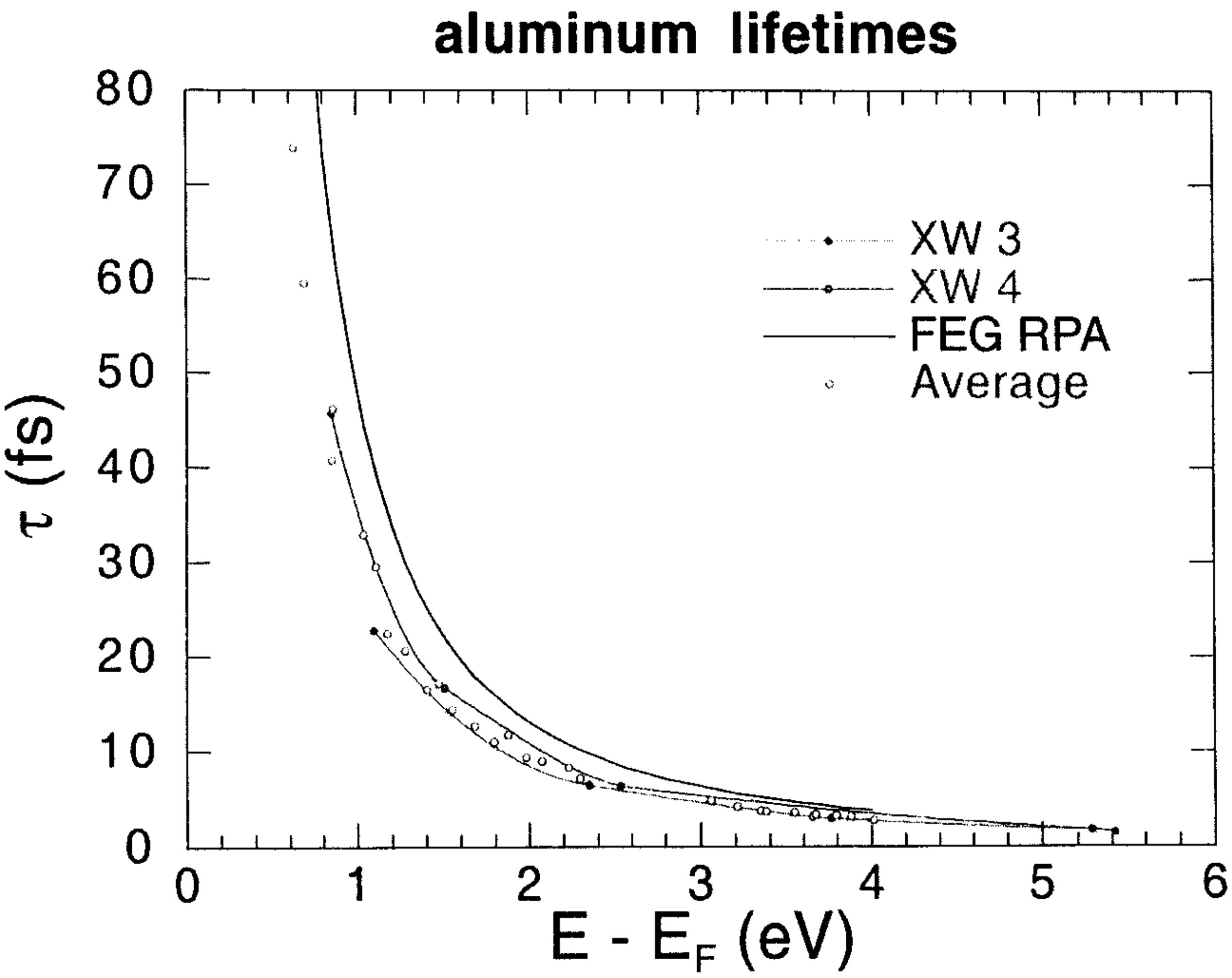
$$B_{if}(\mathbf{q}) = \langle \phi_{\mathbf{k},i} | \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot\mathbf{r}} | \phi_{\mathbf{k}-\mathbf{q},f} \rangle.$$

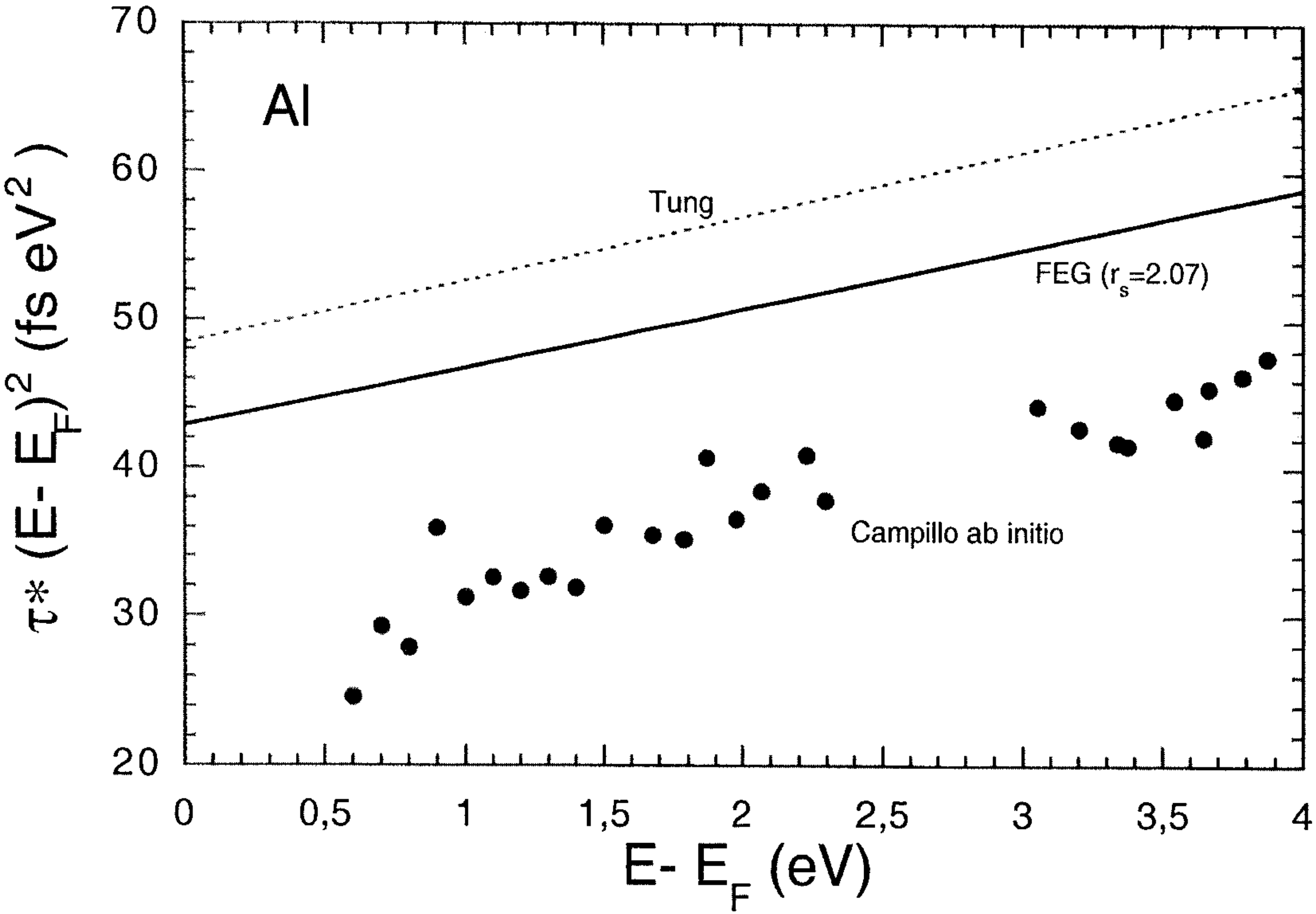
- RPA DIELECTRIC FUNCTION

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G},\mathbf{G}'} - \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\ \chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

- DENSITY RESPONSE FUNCTION

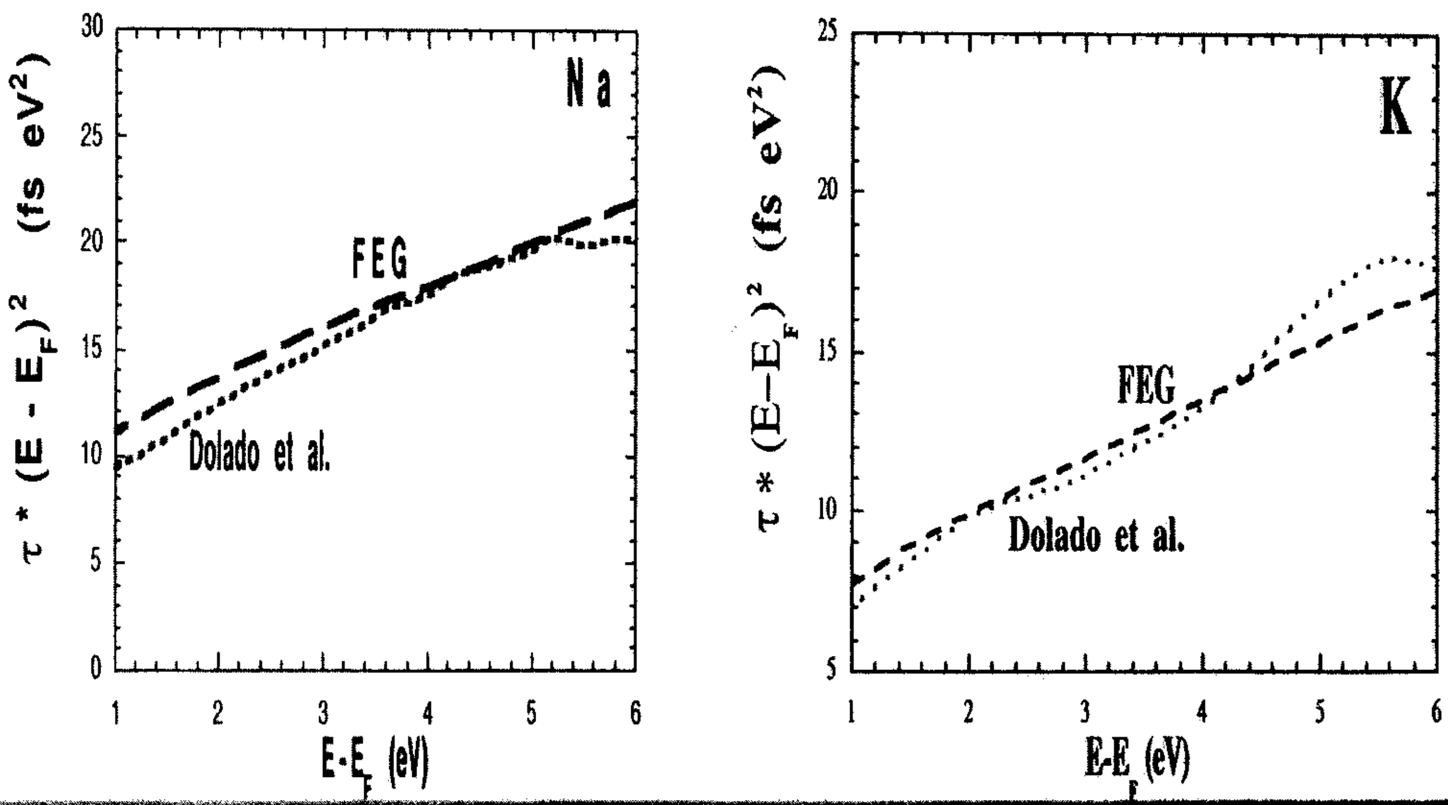
$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \Omega^{-1} \int_{BZ} \mathrm{d}\mathbf{q} \sum_n \sum_{n'} (f_{\mathbf{k},n} - f_{\mathbf{k}+\mathbf{q},n'})$$
$$\times \frac{\langle \phi_{\mathbf{k},n} | e^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \phi_{\mathbf{k}+\mathbf{q},n'} \rangle \langle \phi_{\mathbf{k}+\mathbf{q},n'} | e^{\mathrm{i}(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} | \phi_{\mathbf{k},r}}{\varepsilon_{\mathbf{k},n} - \varepsilon_{\mathbf{k}+\mathbf{q},n'} + (\omega + \mathrm{i}\eta)}$$


aluminum lifetimes
τ (fs)
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
E - E_F (eV)
XW 3
XW 4
FEG RPA
Average

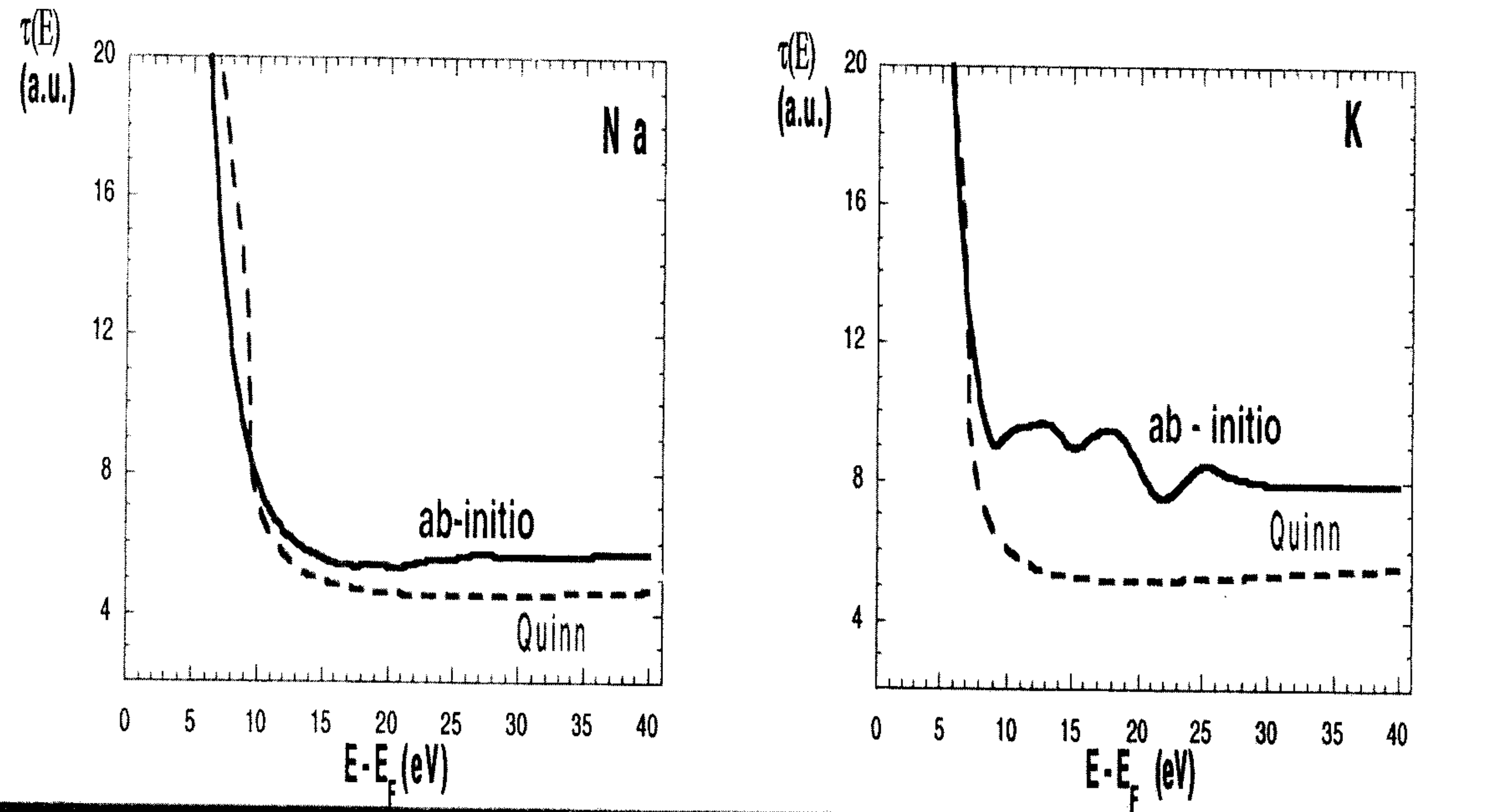


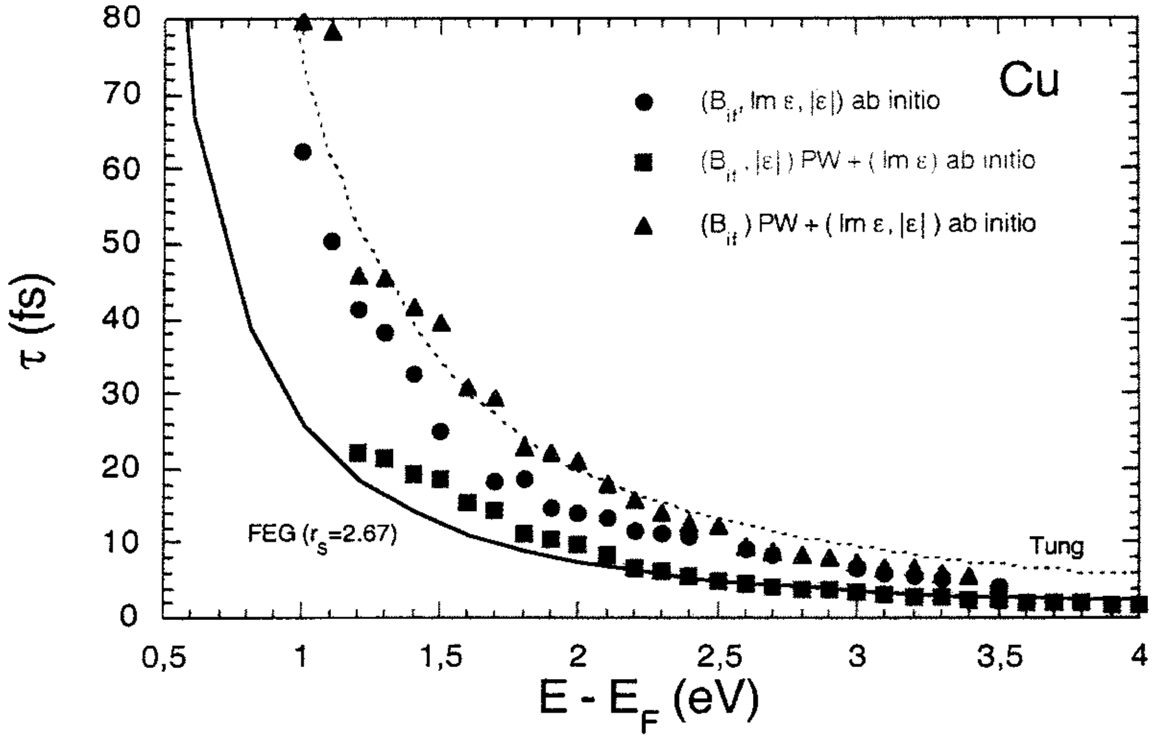
Al
Tung
FEG (r_s=2.07)
Campillo ab initio
τ* (E- E_F)^2 (fs eV^2)
E- E_F (eV)
70
60
50
40
30
20
0
0,5
1
1,5
2
2,5
3
3,5
4

Averaged lifetimes of hot electrons in alkalis



Lifetimes of hot electrons in alkalis

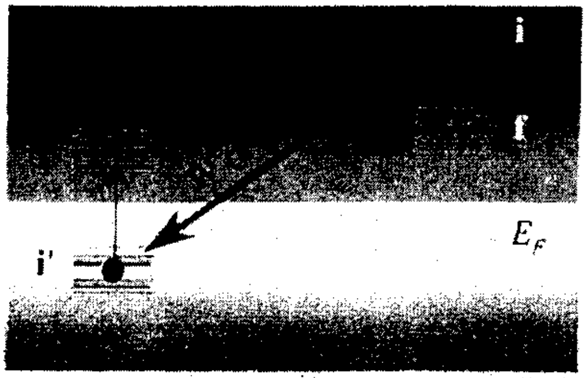




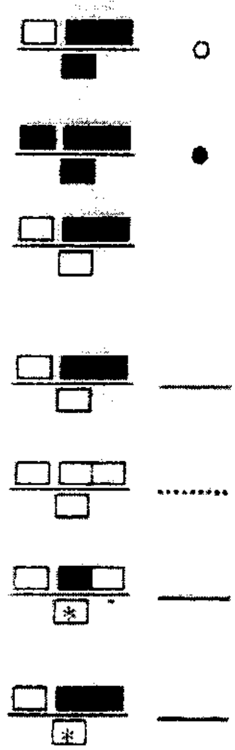
$$\tau^{-1} = \frac{1}{\pi^2} \sum_f{}' \int_{BZ} d\mathbf{q} \sum_{\mathbf{G}} \frac{\left|B_{if}(\mathbf{q}+\mathbf{G})\right|^2}{|\mathbf{q}+\mathbf{G}|^2} \times \frac{\mathrm{Im}\left[\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)\right]}{|\epsilon_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)|^2}.$$

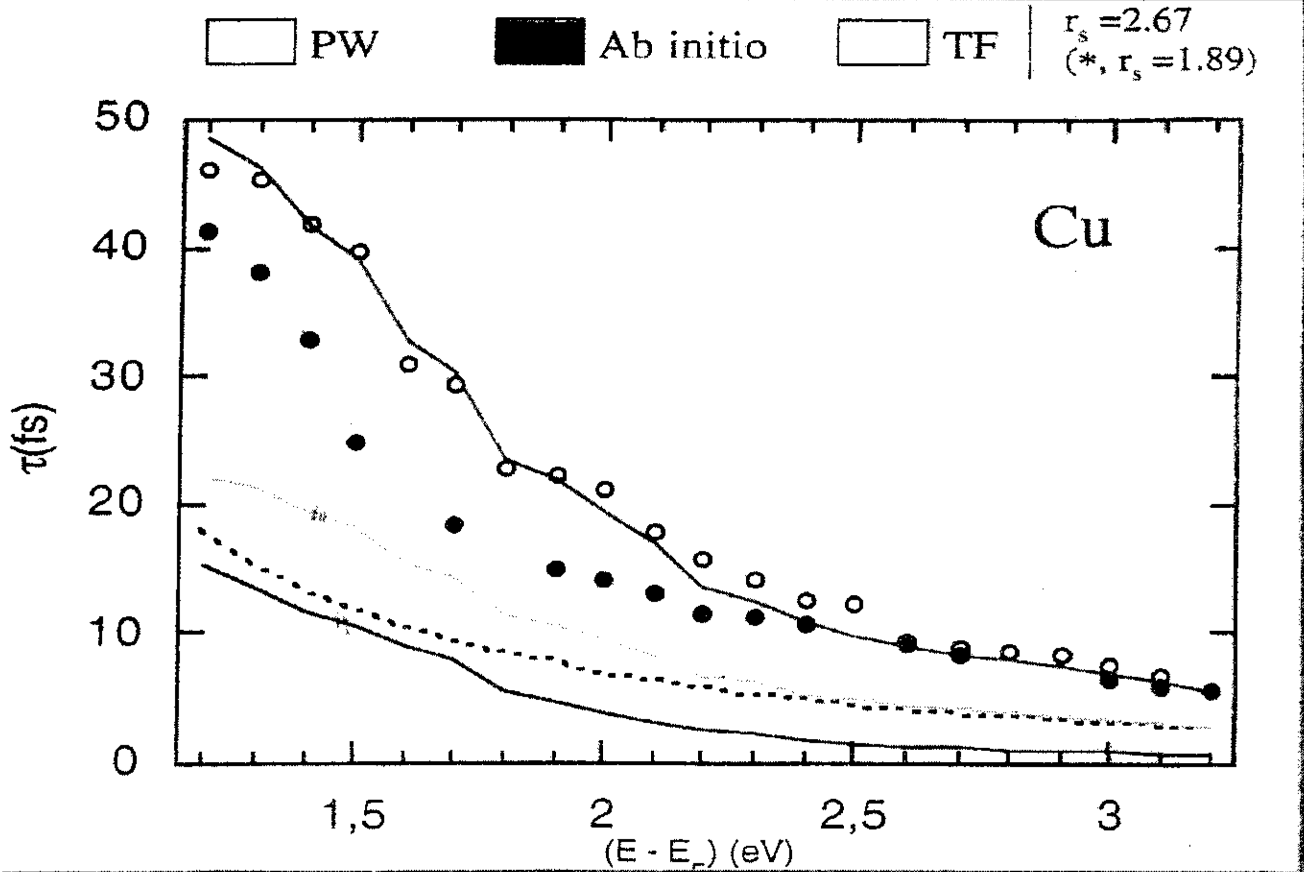
B_{if}	$\mathrm{Im}[\epsilon_{G,G}]$	$\lvert\epsilon_{G,G}\rvert$	figure
PW	PW	PW	___ (RPA)
ab initio	*ab initio*	*ab initio*	●
PW	*ab initio*	PW	■
PW	*ab initio*	*ab initio*	▲

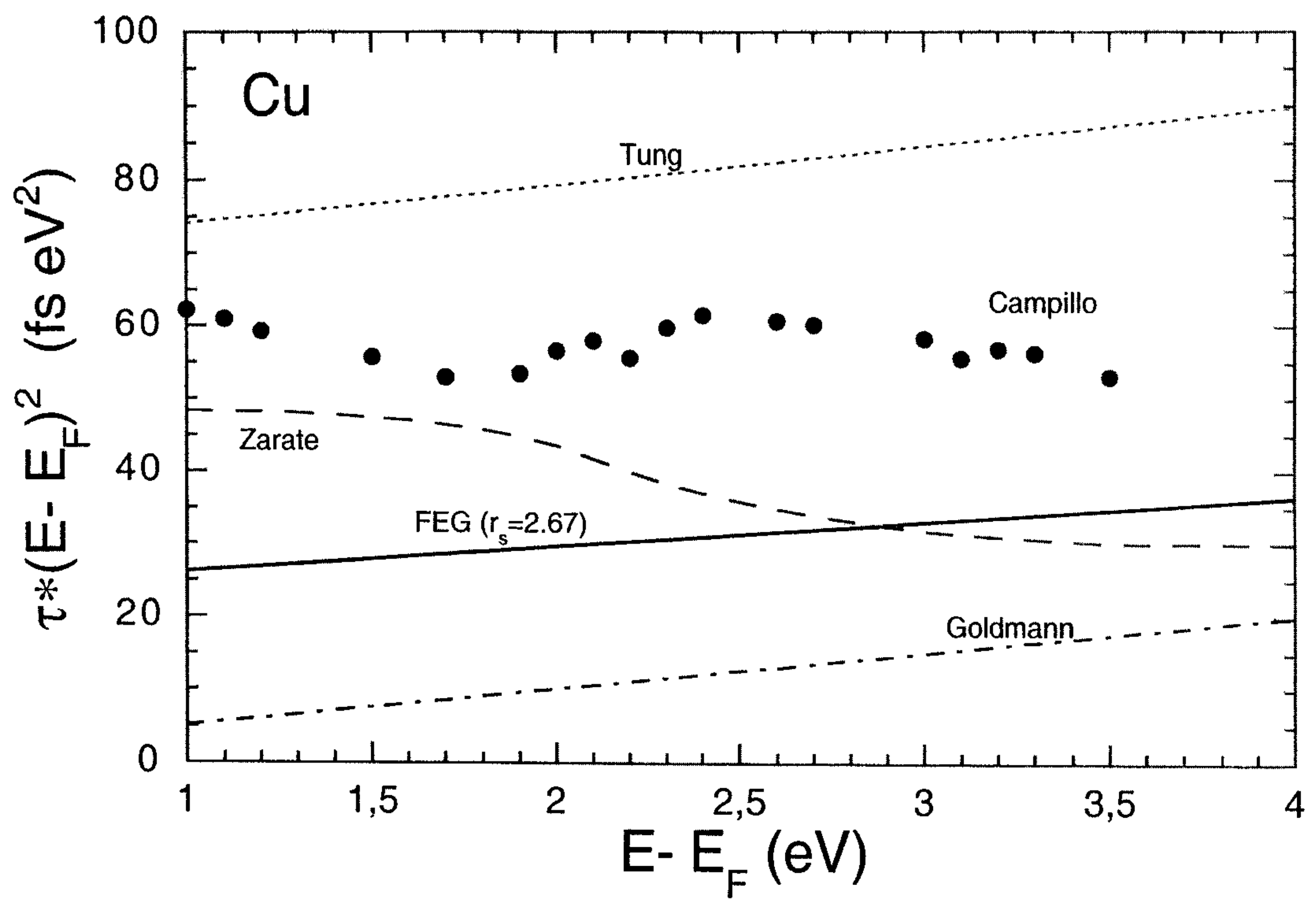
Hot electrons in Cu

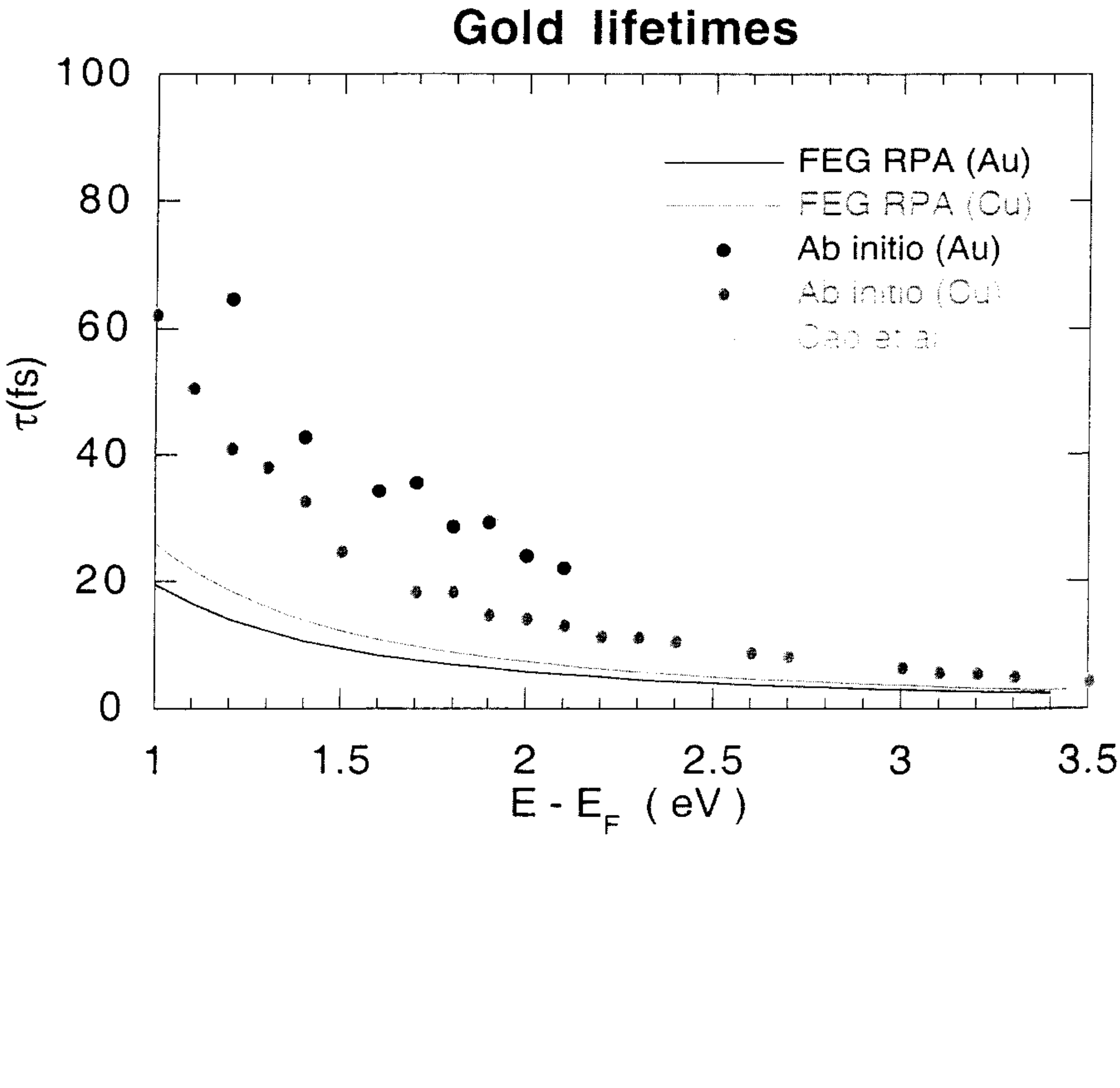


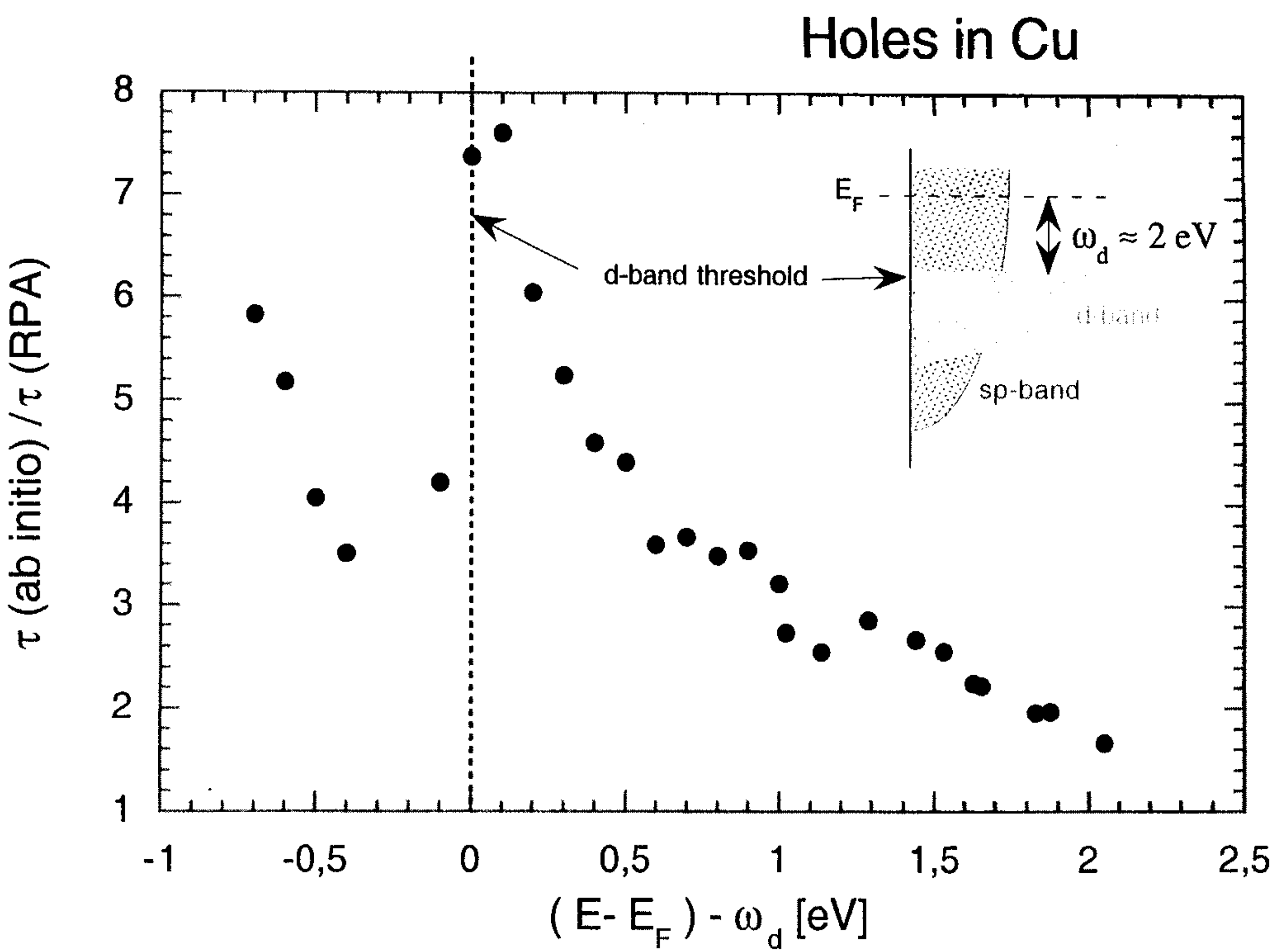
$$\tau^{-1} = \frac{\text{Coupling } i \to f \quad \text{Coupling } i' \to f'}{\text{Screening}}$$

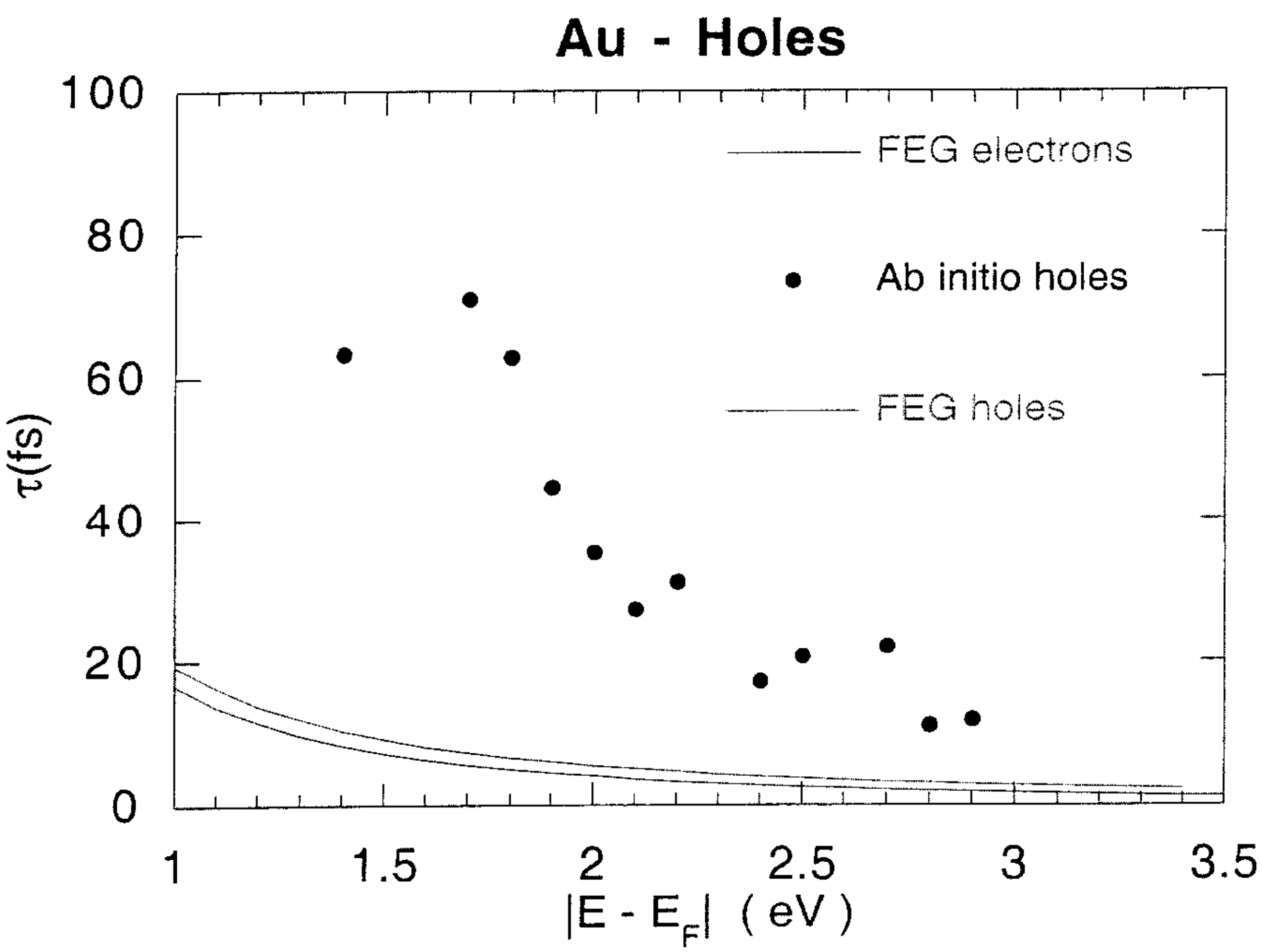




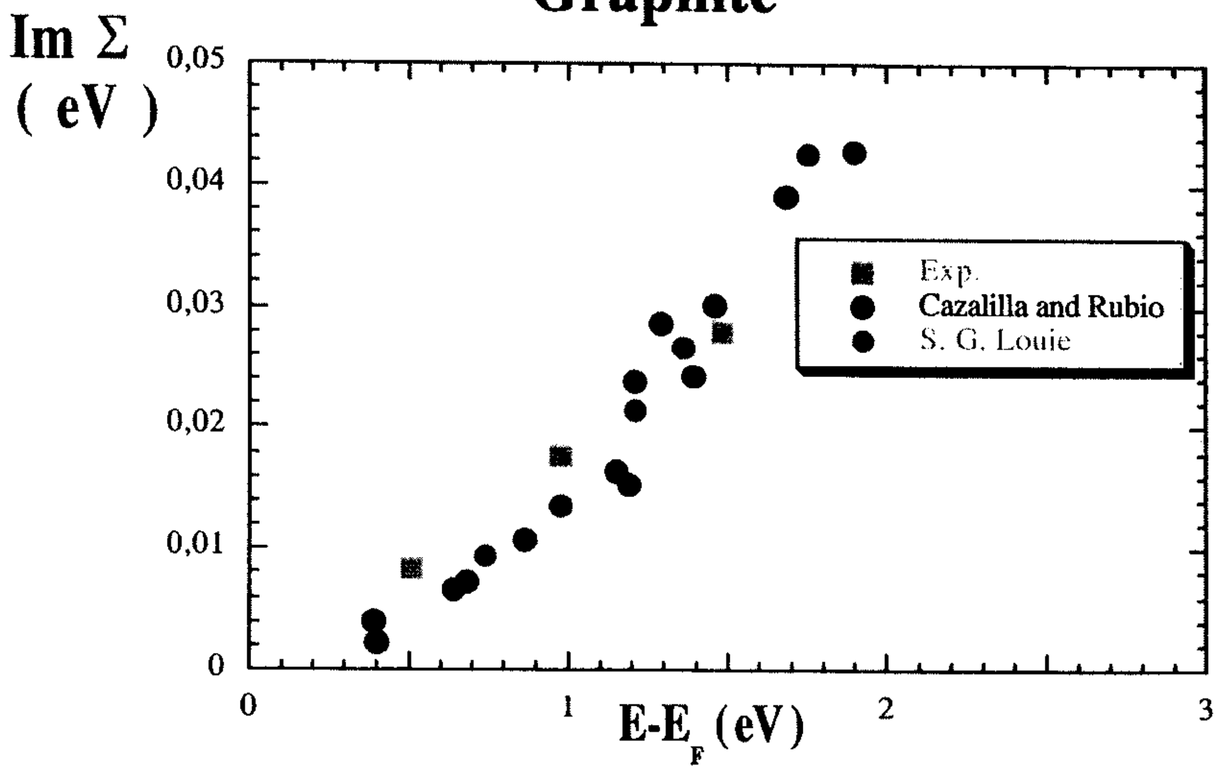

Cu
Tung
Campillo
Zarate
FEG (r_s=2.67)
Goldmann
τ*(E- E_F)^2 (fs eV^2)
E- E_F (eV)
100
80
60
40
20
0
1
1,5
2
2,5
3
3,5
4


Gold lifetimes
FEG RPA (Au)
FEG RPA (Cu)
Ab initio (Au)
Ab initio (Cu)
τ(fs)
E - E_F (eV)
100
80
60
40
20
0
1
1.5
2
2.5
3
3.5

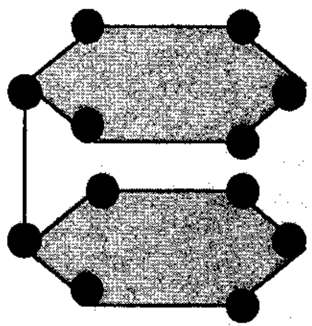

Holes in Cu
τ (ab initio) / τ (RPA)
(E- E_F) - ω_d [eV]
d-band threshold
E_F
ω_d ≈ 2 eV
d-band
sp-band
8
7
6
5
4
3
2
1
-1
-0,5
0
0,5
1
1,5
2
2,5


Au - Holes
FEG electrons
Ab initio holes
FEG holes
τ(fs)
|E - E_F| (eV)
0
20
40
60
80
100
1
1.5
2
2.5
3
3.5

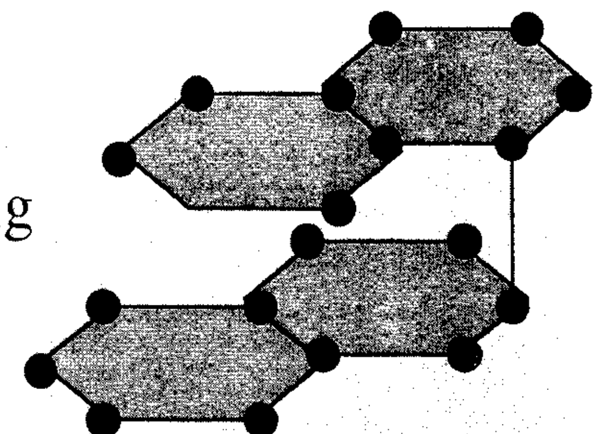
Graphite



AA-
stacking



AB-
stacking

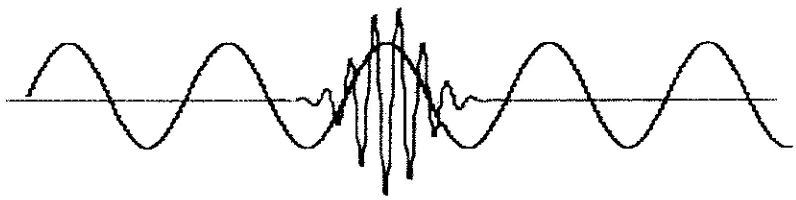


Lifetime of localized states

<u>Extended state</u>

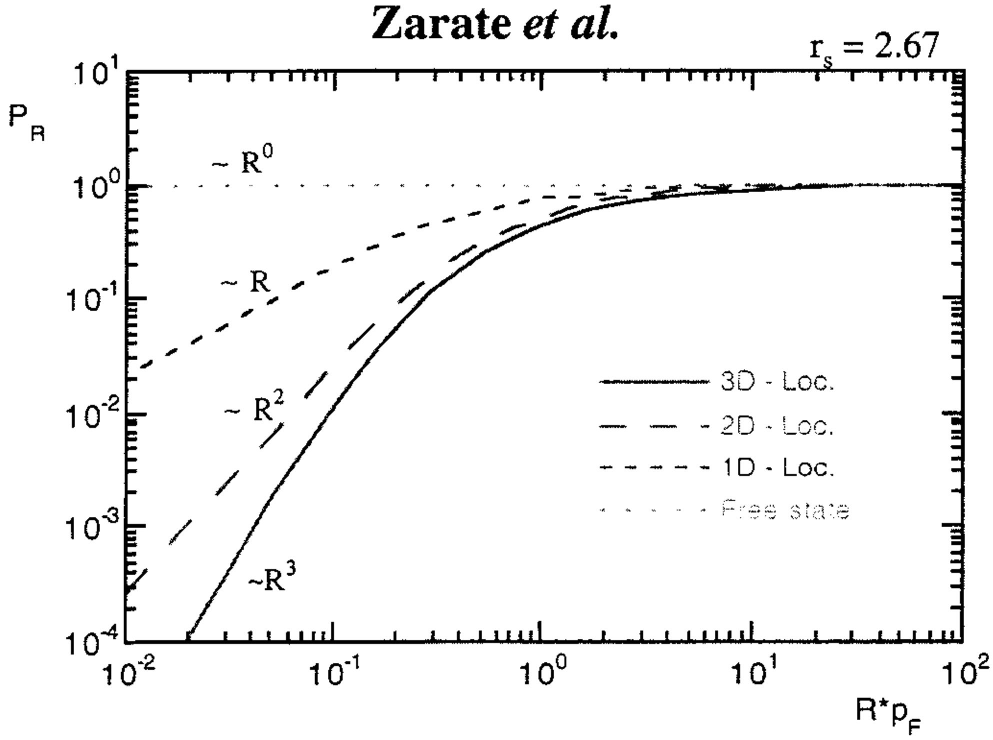
Big overlap => Short lifetimes

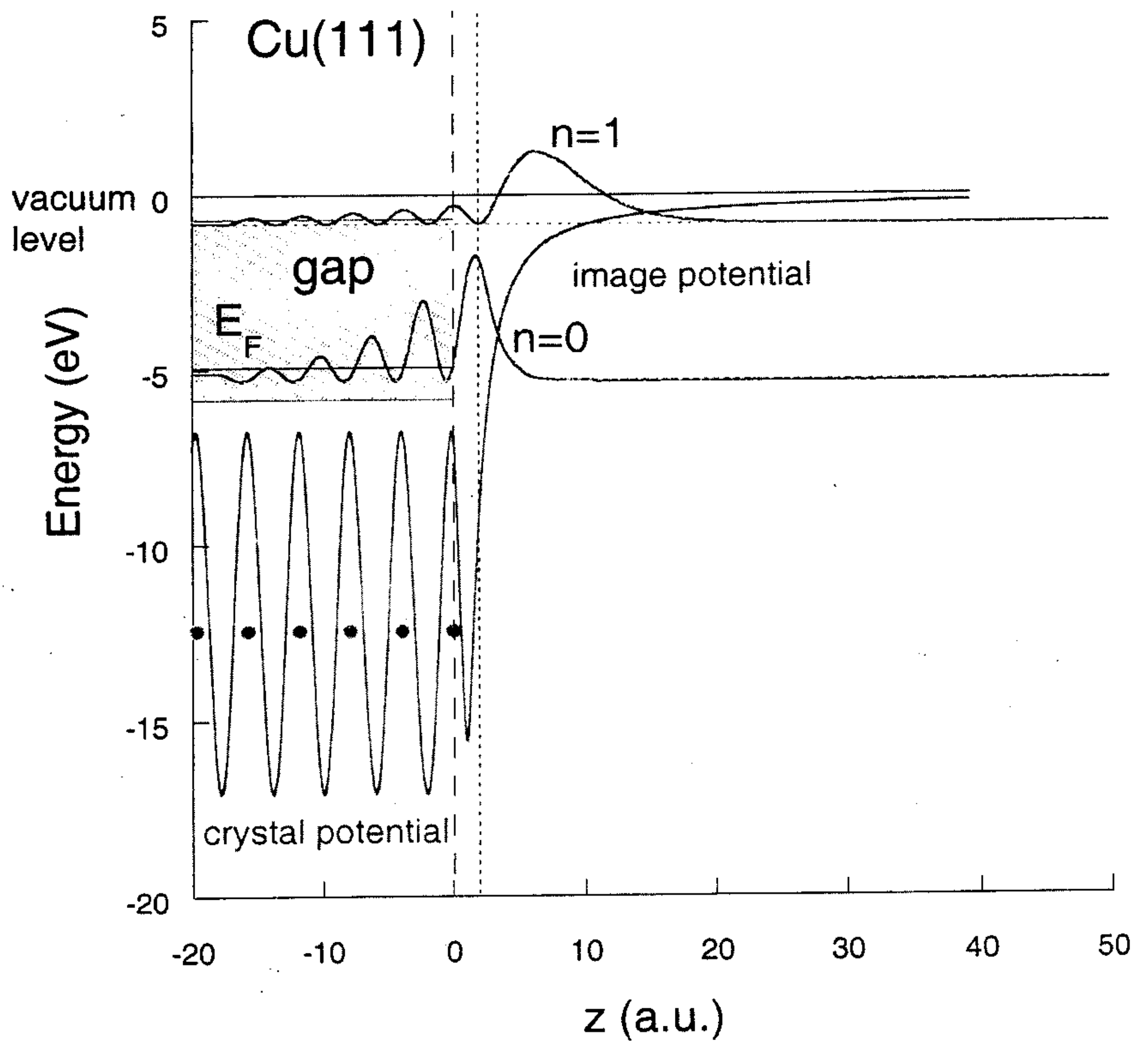
<u>Localized state</u>

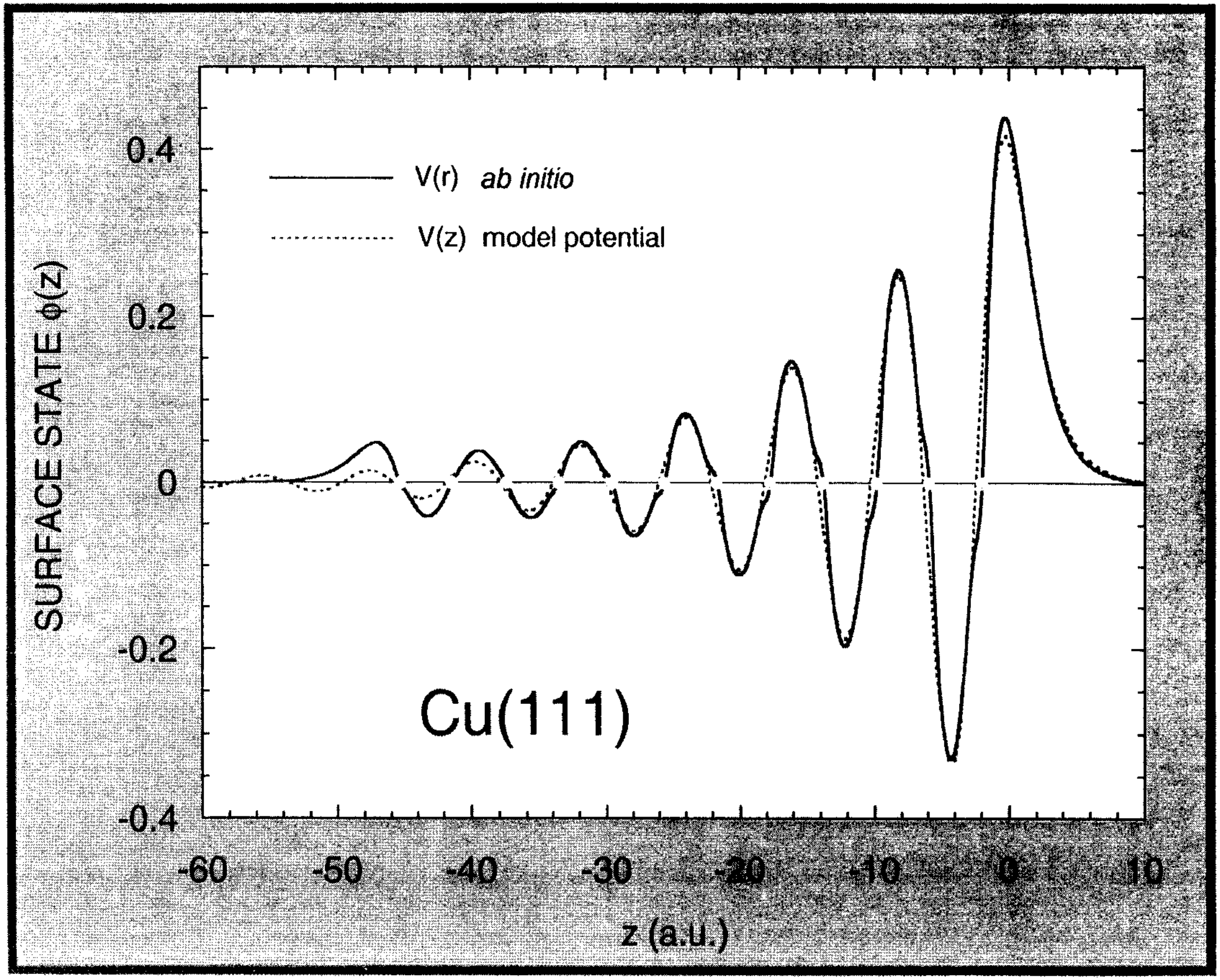


Small overlap => long lifetimes

Zarate *et al.*



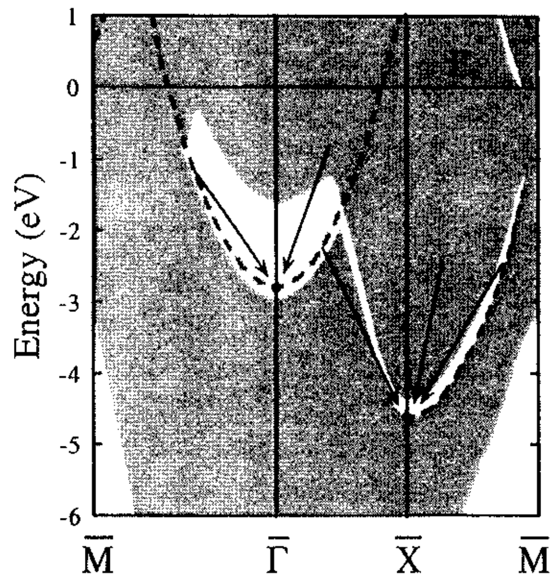

Cu(111)
n=1
vacuum level
gap
image potential
E_F
n=0
Energy (eV)
crystal potential
z (a.u.)


V(r) ab initio
V(z) model potential
Cu(111)
SURFACE STATE φ(z)
0.4
0.2
0
-0.2
-0.4
-60
-50
-40
-30
-20
-10
0
10
z (a.u.)

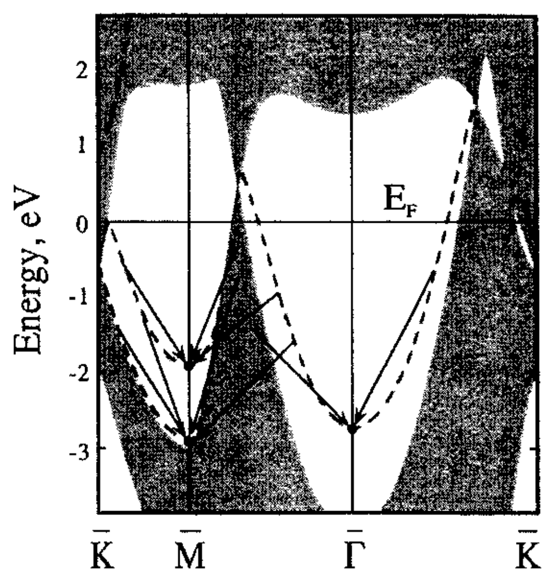
Very often a simplified model throws more light on the real workings of nature than any number of "ab initio" calculations of individual situations, which, even where correct, often contain so much detail as to conceal rather than reveal reality. It can be a disadvantage rather than an advantage to be able to compute or measure too accurately, since often when one measures or computes is irrelevant in terms of mechanism after all, the perfect computation simply reproduces Nature, it does not explain her.

P. W. Anderson (1978) Nobel Lecture

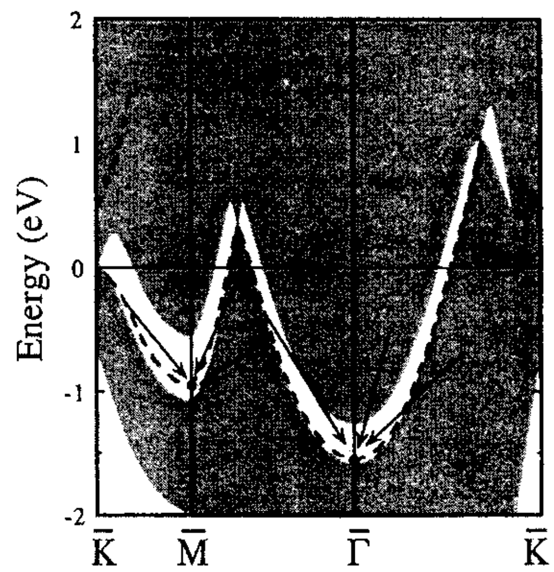
Al(001) Surface Band Structure



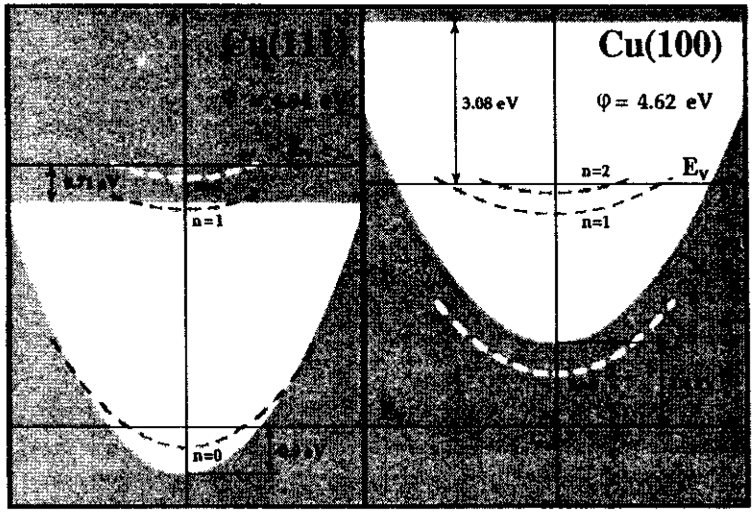
Be(0001) Surface Band Structure



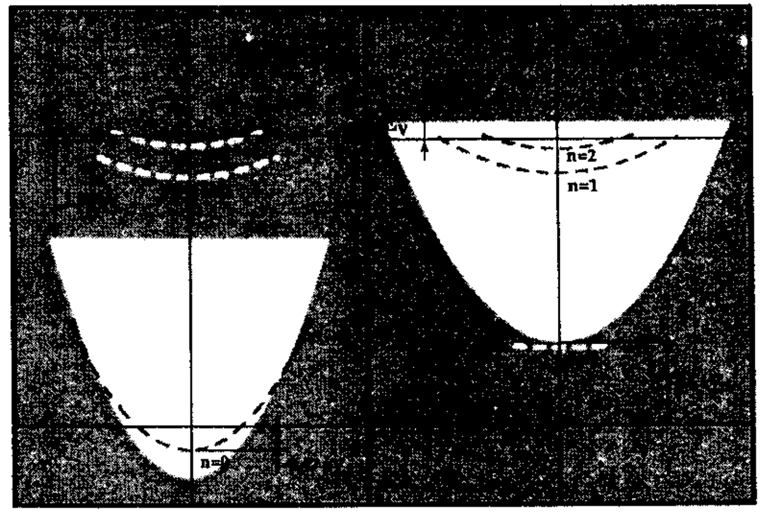
Mg(0001) Surface Band Structure



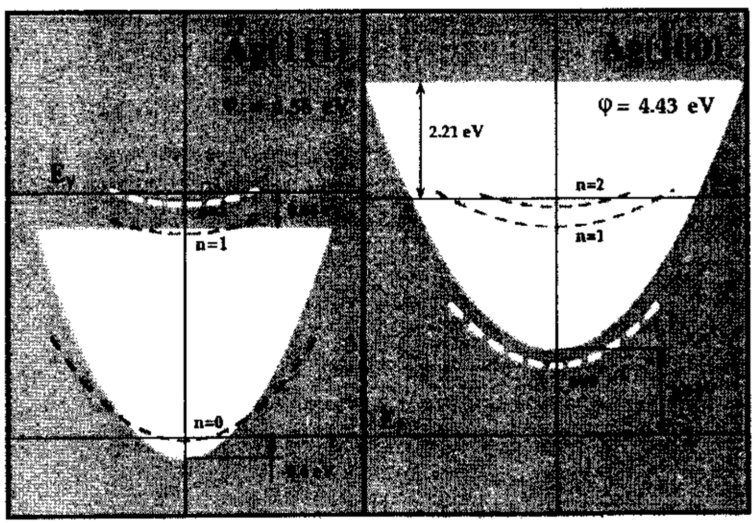
Cu(111) and Cu(100) Surface Band Structure



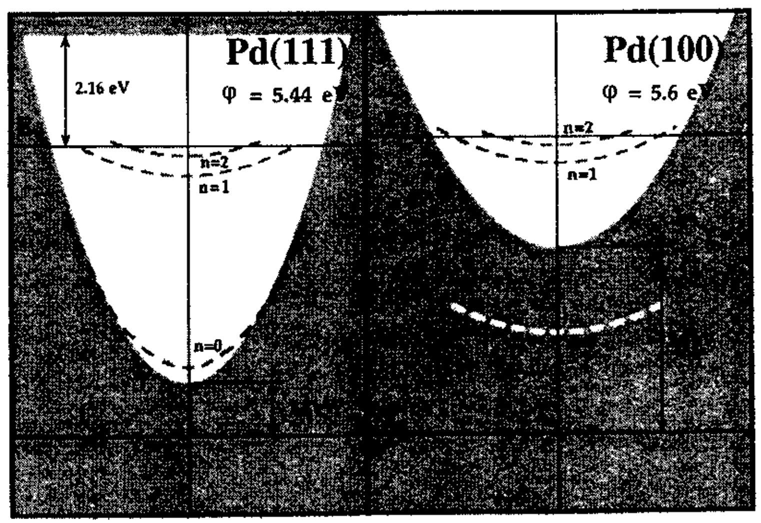
Au(111) and Au(100) Surface Band Structure



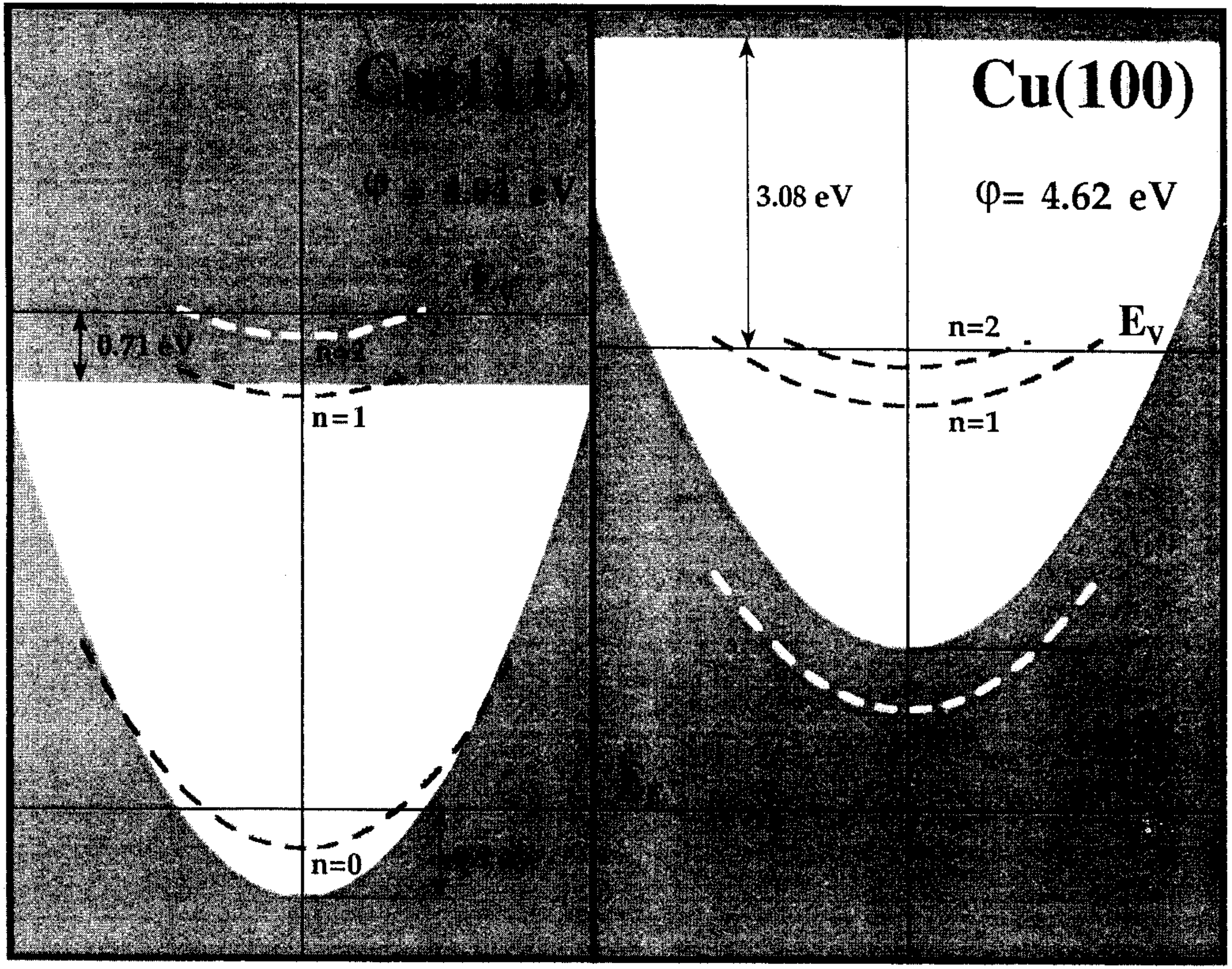
Ag(111) and Ag(100) Surface Band Structure



Pd(111) and Pd(100) Surface Band Structure



Cu(111) and Cu(100) Surface Band Structure

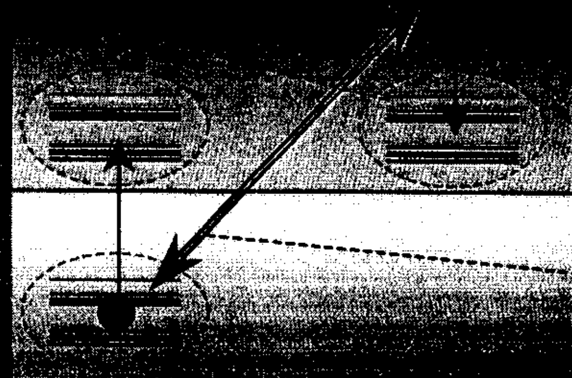


Density Of States vs. Screening

Density of states

More DOS

Shorter lifetimes



Screening

More DOS

Longer lifetimes

3D (Quinn 1962)

$$\tau \approx \frac{263.3 \cdot r_S^{-5/2}}{(E-E_F)^2}\ [fs]$$

$$\approx \frac{1.97 \cdot E_F^{5/4}}{(E-E_F)^2}\ [fs]$$

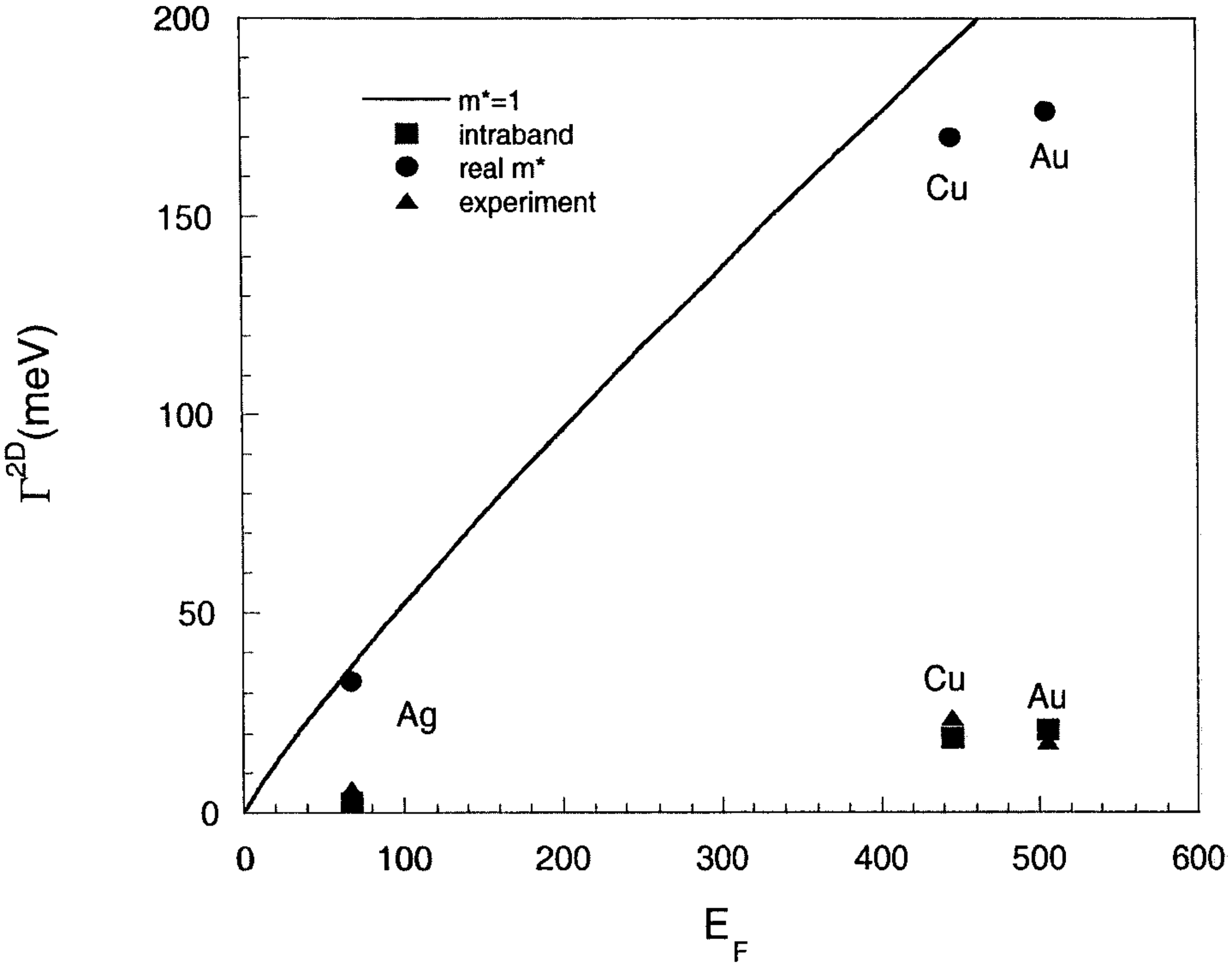
2D (Giuliani, Quinn 1982)

$$\tau \approx \frac{16.6 \cdot E_F}{(E-E_F)^2}$$

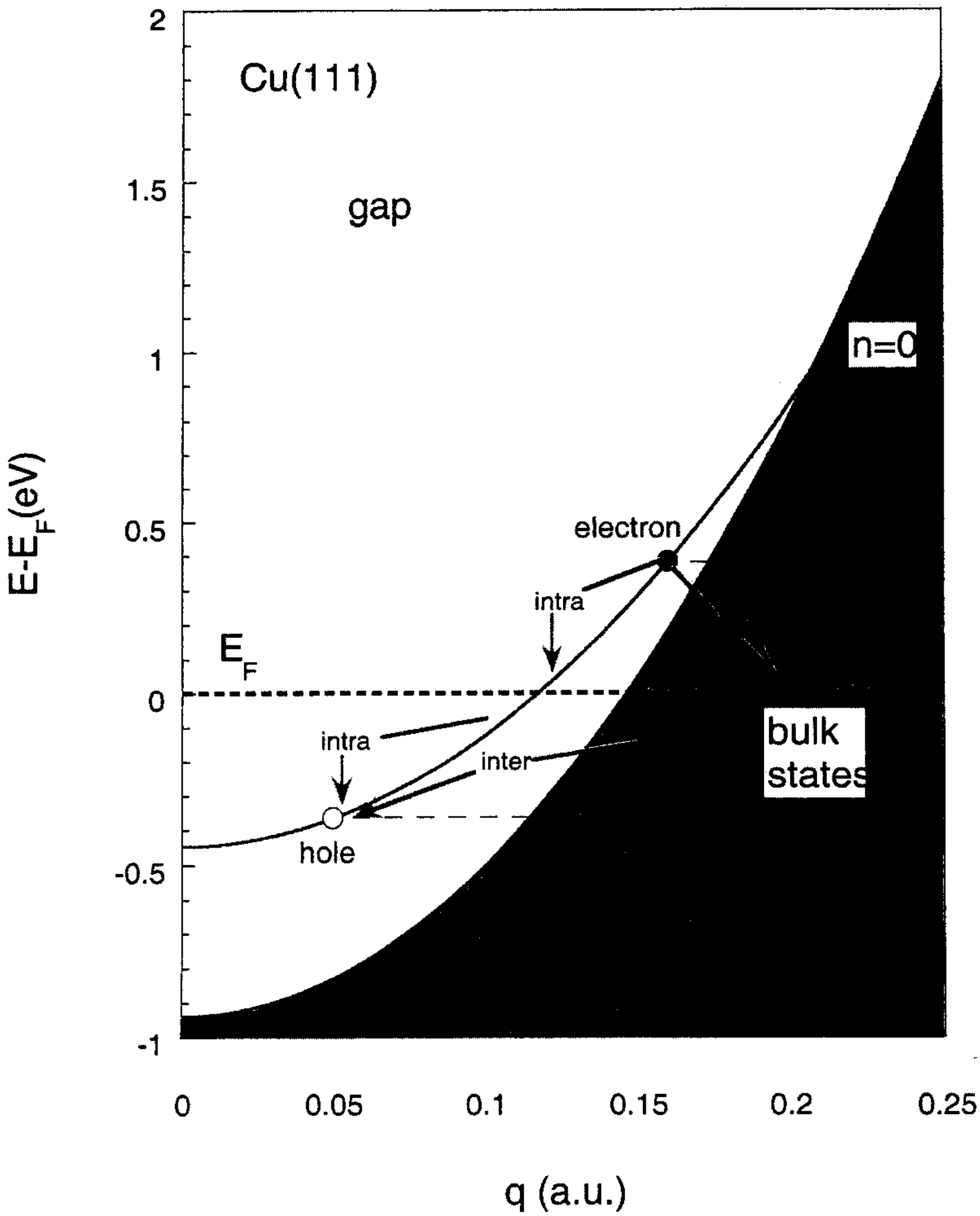
$$\times [6.4 - \ln(E_F / m^*) + 2\ln(\tfrac{E-E_F}{E_F})]^{-1}\ [fs]$$

(r_S and m^* in a.u.;Energy in eV)

2D LINEWIDTH AT GAMMA POINT



Cu(111) band structure



Experiments vs. theory

◆ Holes ($\bar{\Gamma}$) : Theilemann et al. (1997) ; Kliewer et al. (2000)

Theoretical models (3D electron gas) predict significantly longer lifetimes than are observed with STM and photoelectron spectroscopy

FLT: longer lifetimes: factors of 4 in Cu (111)

◆ Electrons (Γ): Burgi et al. PRL (1994)

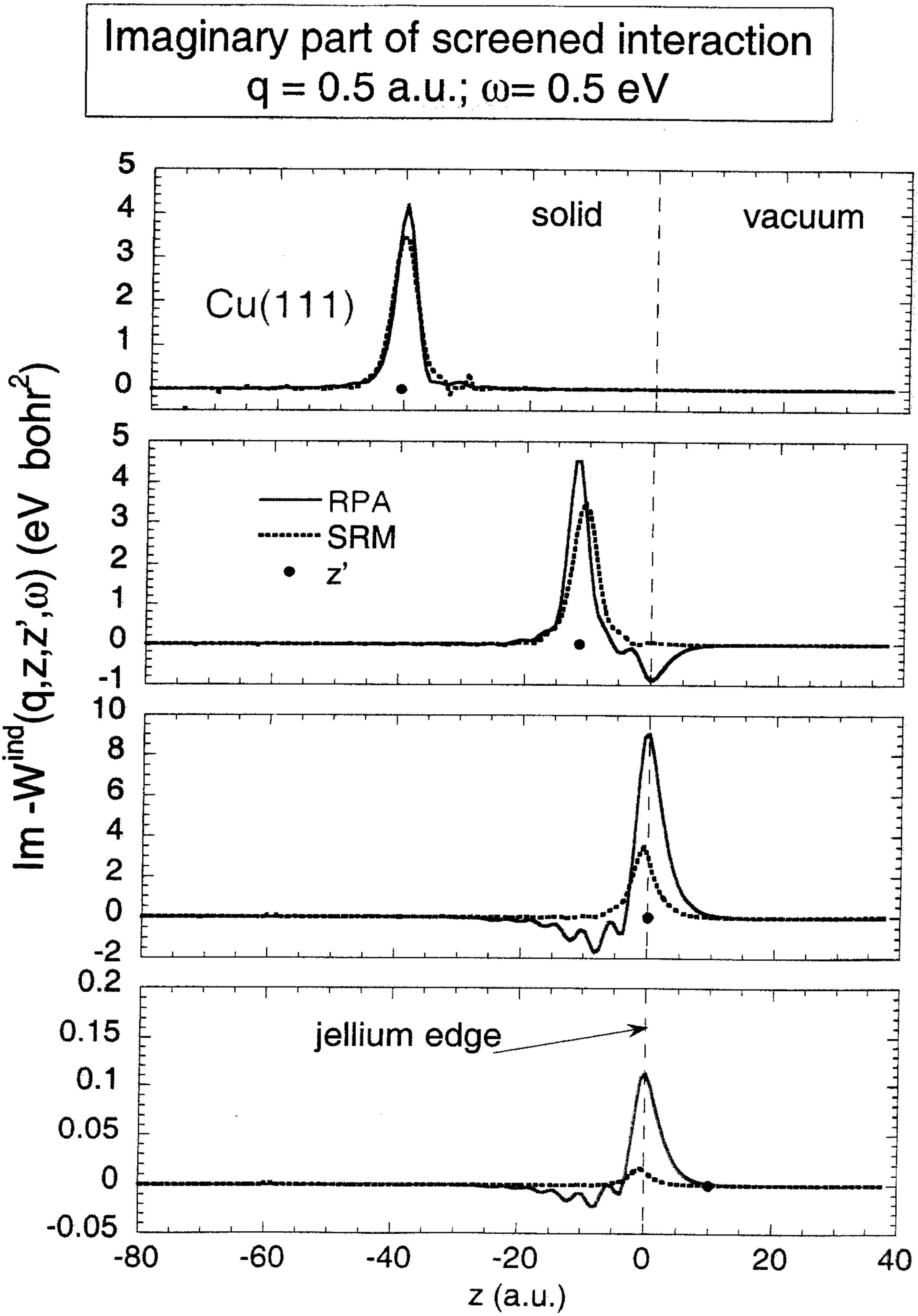
"Experimental values are comparable to the corresponding bulk electron lifetimes.
This indicates that electron-electron interaction of hot surface state electrons with the Fermi sea is dominated by the underlying bulk electrons."

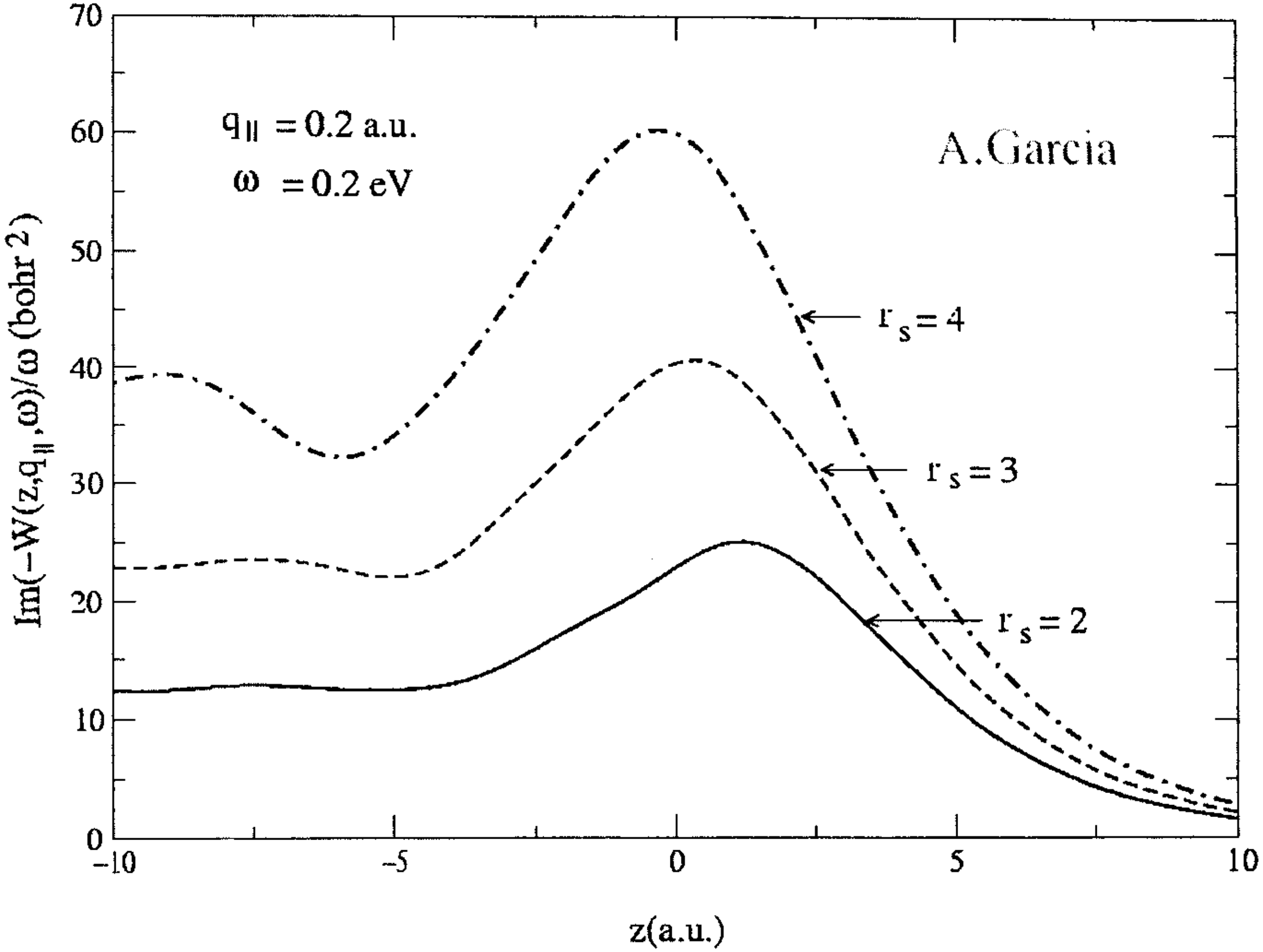
FLT: longer lifetimes (~ 30%)

$\tau.\Delta^2 \sim 17.1$ (22.4 fs) in Cu (111)

New physical picture

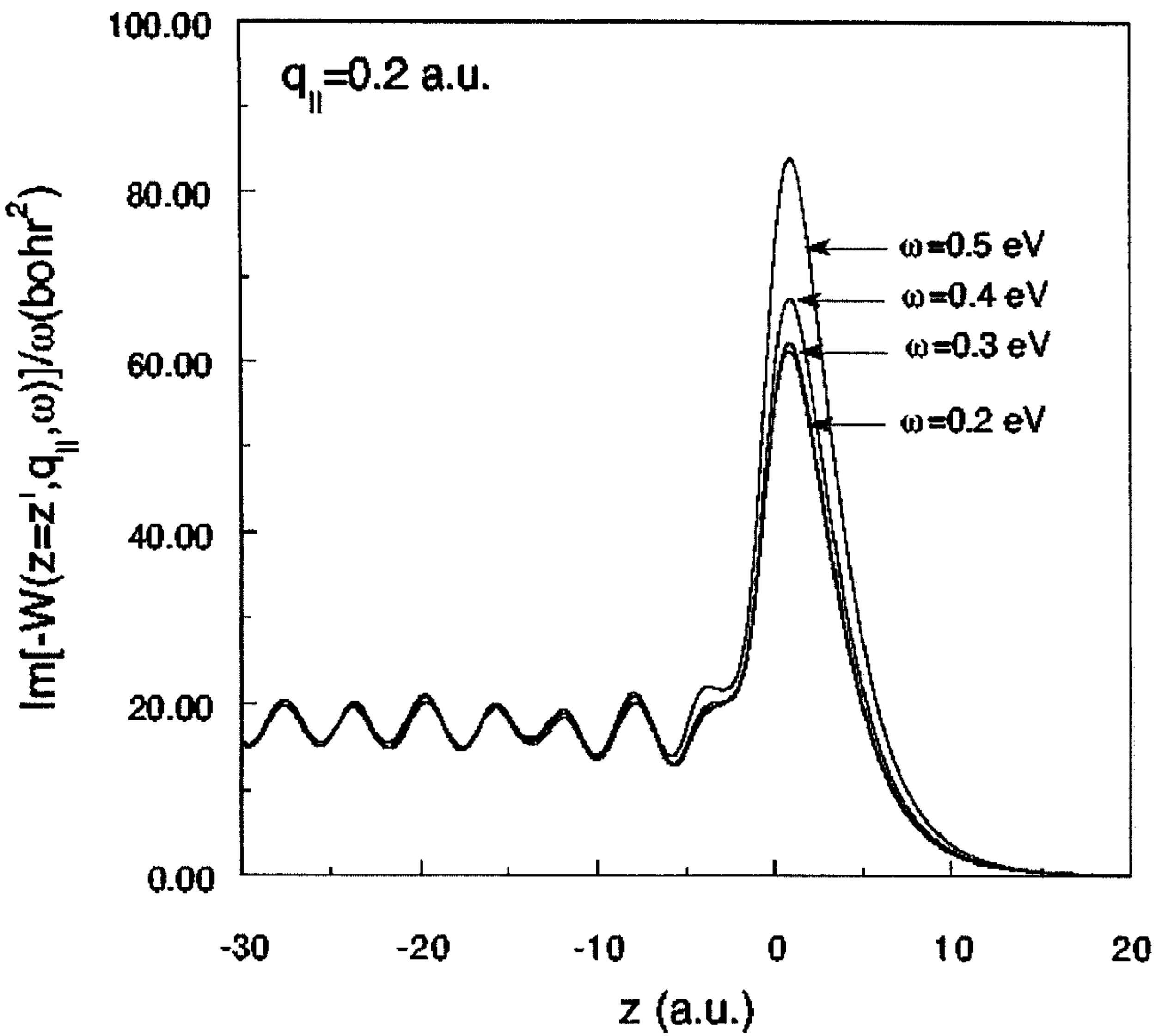
New physical picture to emerge has two-dimensional decay channels contributing in an important manner (dominating in the case of holes) to electron-electron interaction that contribute to the decay, screened by the electron states of the underlying three-dimensional electron system


Imaginary part of screened interaction
q = 0.5 a.u.; ω= 0.5 eV
solid
vacuum
Cu(111)
RPA
SRM
z'
jellium edge
Im -W^ind(q,z,z',ω) (eV bohr^2)
z (a.u.)



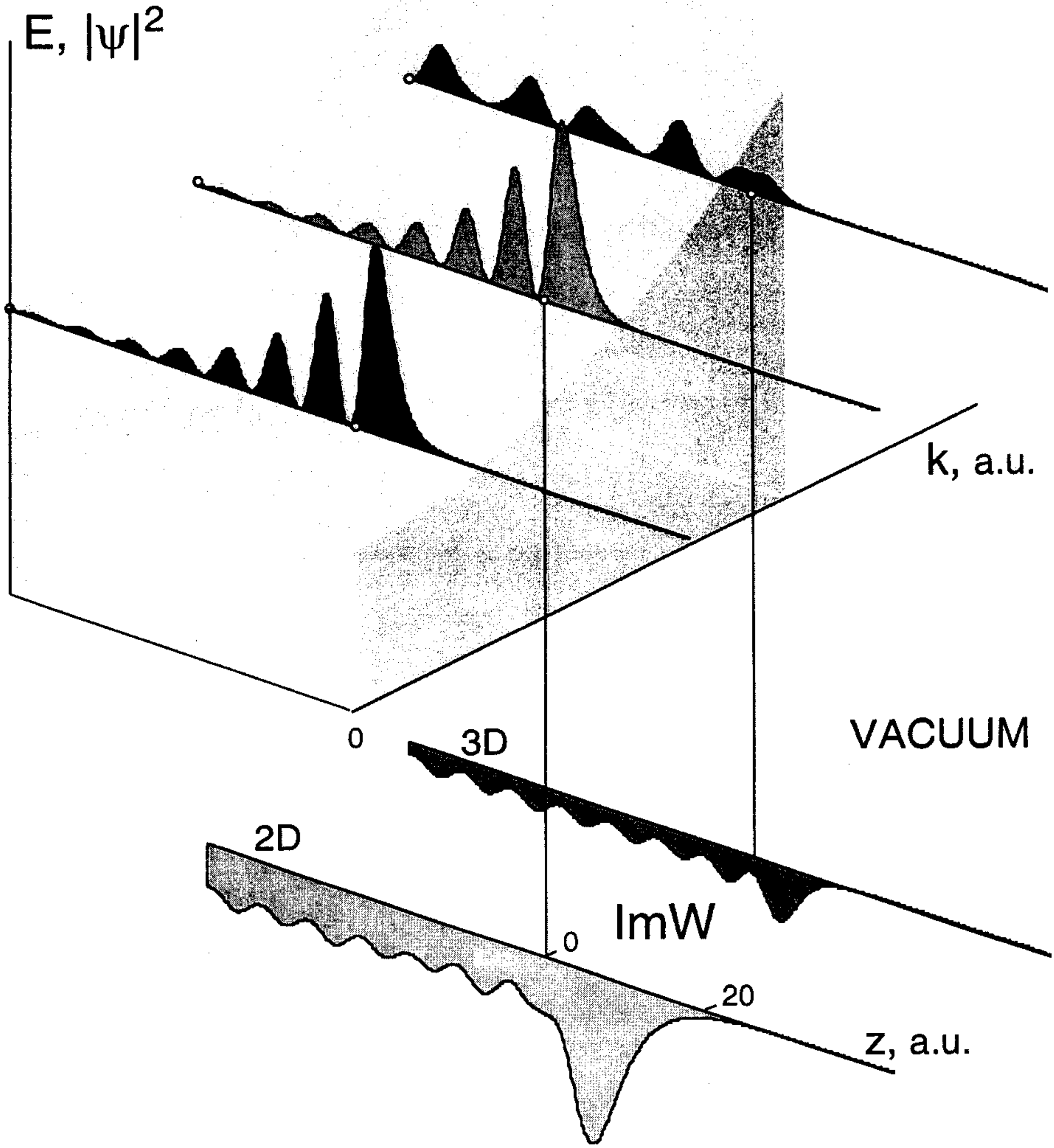
A.Garcia
$q_{\|} = 0.2$ a.u.
$\omega = 0.2$ eV
$r_s = 4$
$r_s = 3$
$r_s = 2$
$Im(-W(z,q_{\|},\omega)/\omega$ (bohr ^{2})
z(a.u.)

Cu(111)

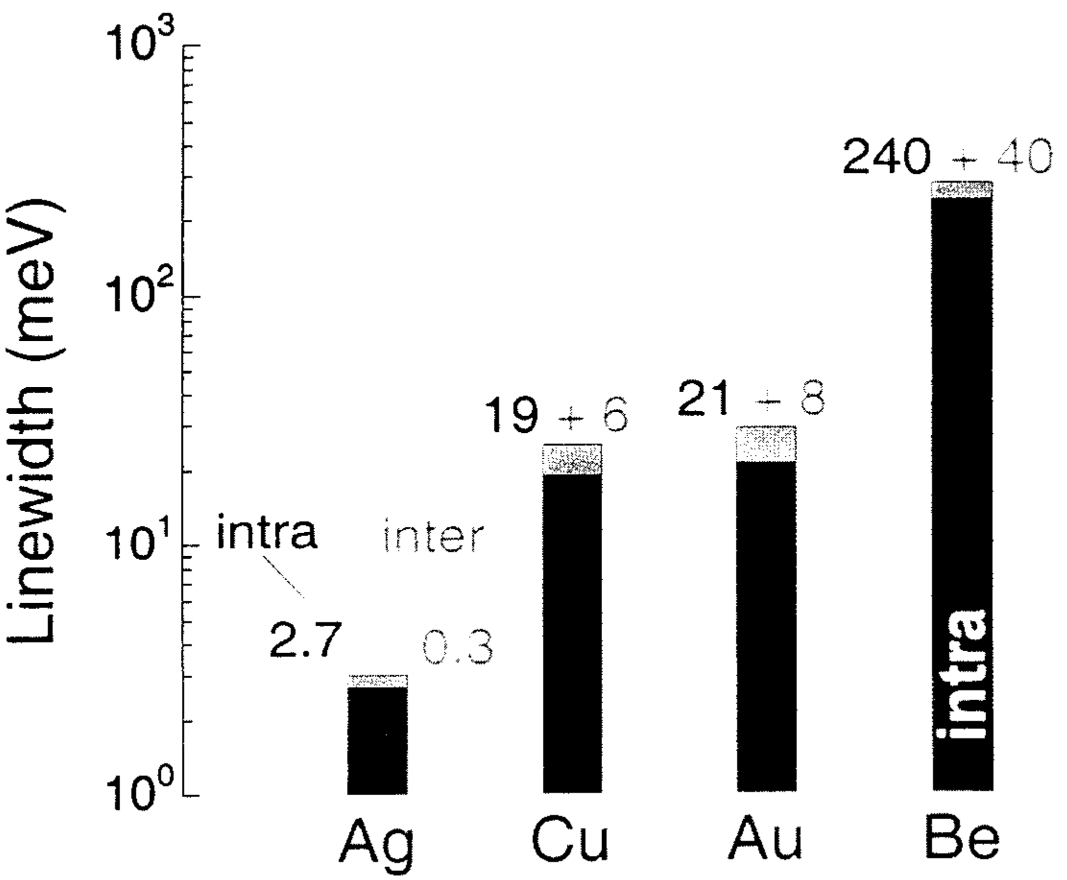


$q_{\parallel}$=0.2 a.u.
ω=0.5 eV
ω=0.4 eV
ω=0.3 eV
ω=0.2 eV
100.00
80.00
60.00
40.00
20.00
0.00
Im[-W(z=z',q$_{\parallel}$,ω)]/ω(bohr^2)
-30
-20
-10
0
10
20
z (a.u.)

Imaginary Part of the Screened Interaction for Surface and Bulk Transitions



Intrinsic surface state at Γ point
(Model potential calculation *)



* *San Sebastian group*

	Ag	Cu	Au	Be
E_B (meV)	65	445	505	2800
m*	0.44	0.42	0.28	1.5

Line widths Γ (meV) - (1 1 1) faces - $\bar{\Gamma}$ hole

	Experiment		Phonons (Debye)		Theory	
	STM	PES	Bulk	Surface	Old	New
Ag	6	20	5.2	4.7	5.3	7.2
Au	18	60	5.2	4.7	8.6	18.9
Cu	24	21 *	8	7.6	10.2	21.7

* Obtained by exploiting and observed correlation with LEED spot profile to extrapolate the PES line width to zero defect density (Theilmann et al. (1997))

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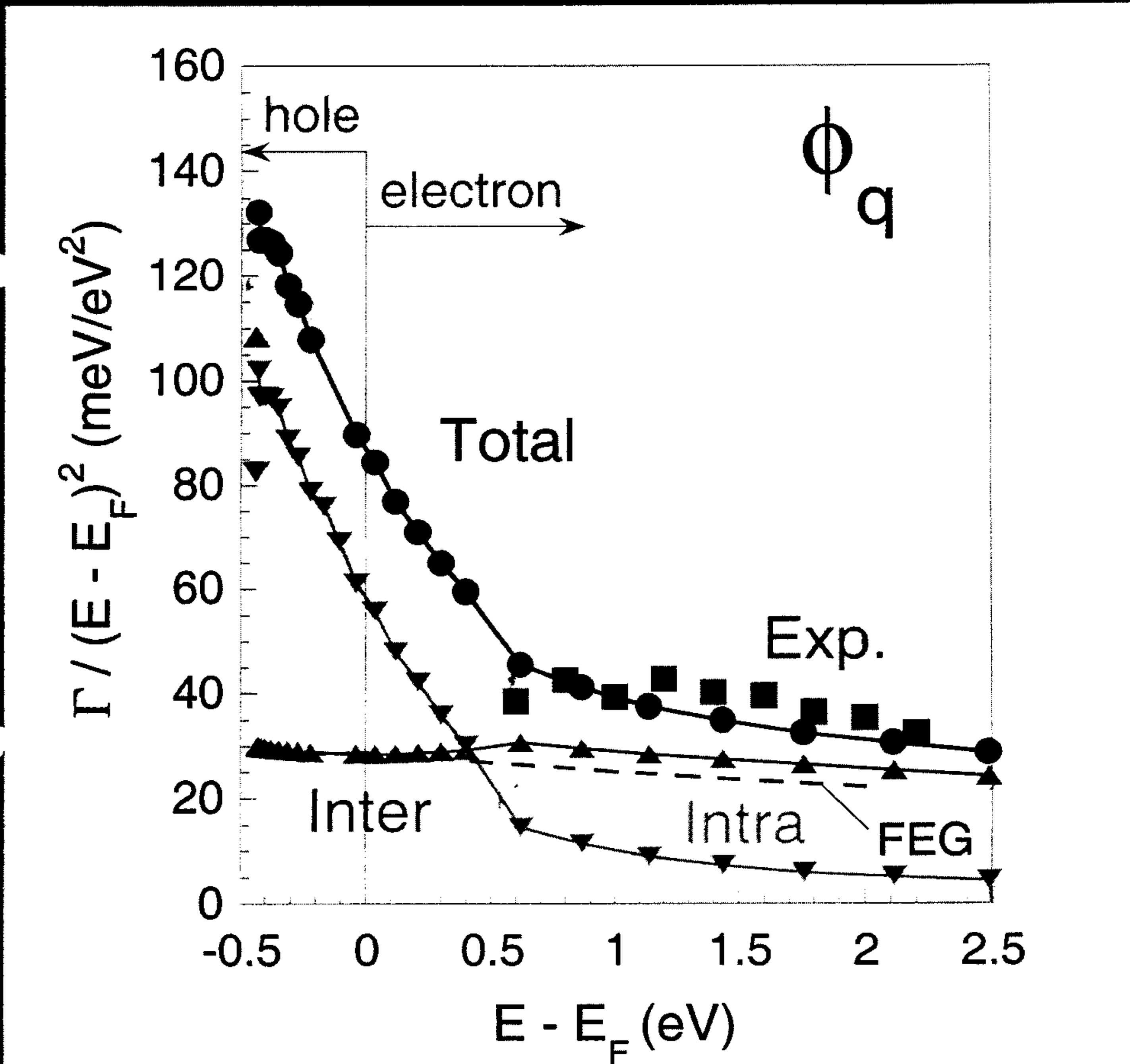
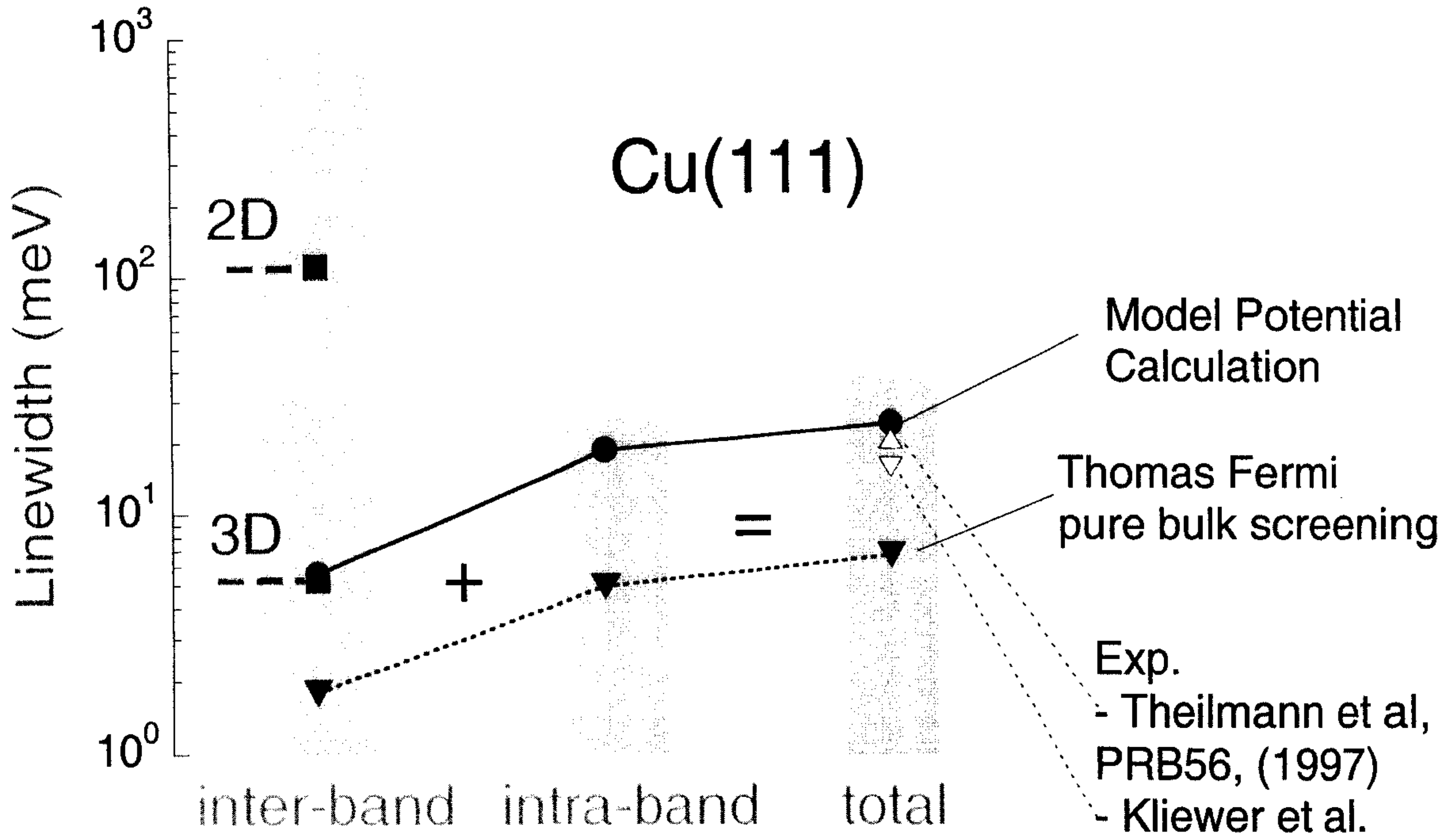
Linewidth of intrinsic surface state on Cu(111)

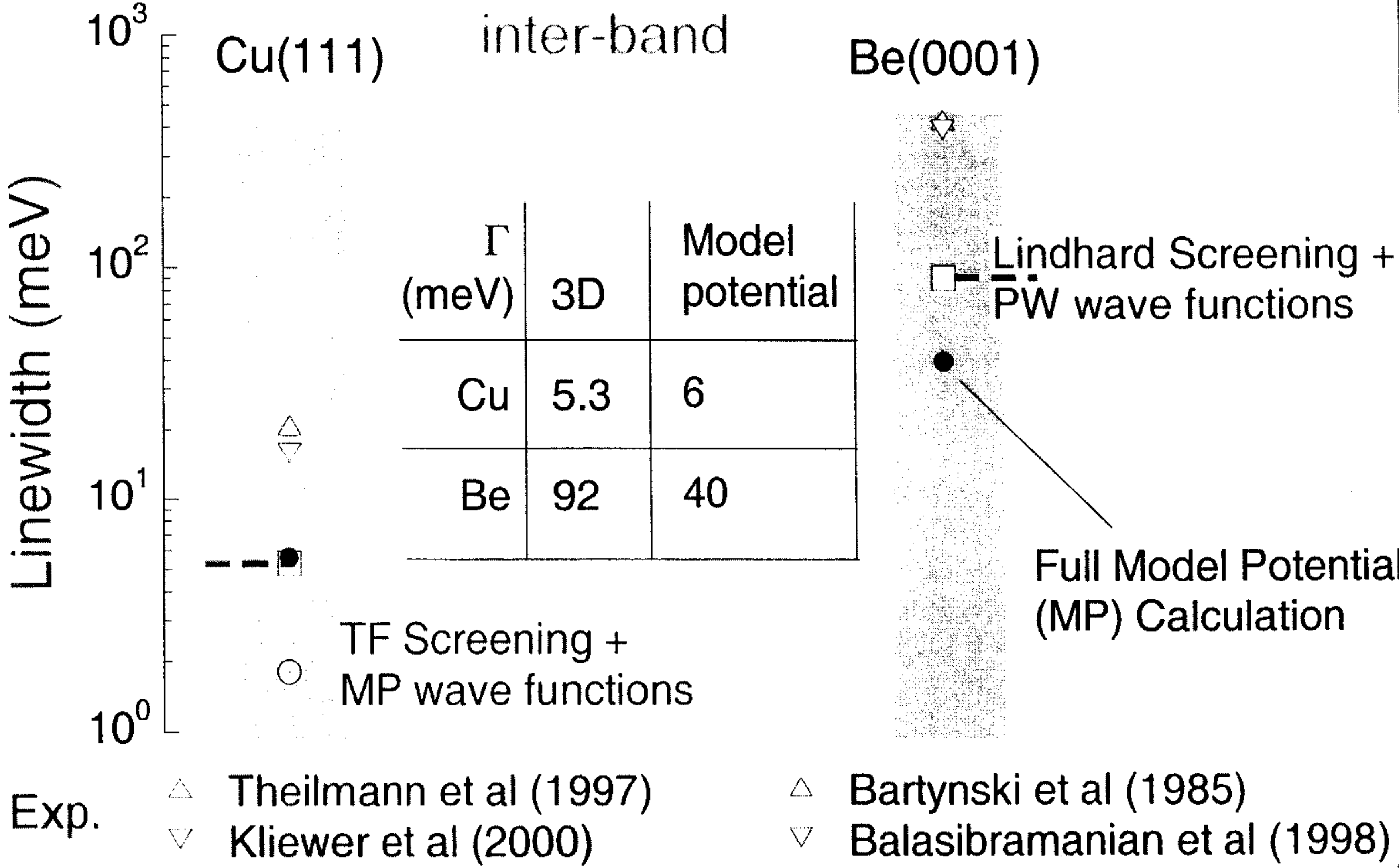


Exp.: ■ Bürgi *et al*, (1999);
▲ [e-e] Theilmann *et al*, (1997);
▼ [e-e] Kliewer *et al*. (2000).
Theory: Model potential calculation and FEG (PW, 3D).

Linewidth of intrinsic surface state at $\bar{\Gamma}$ point

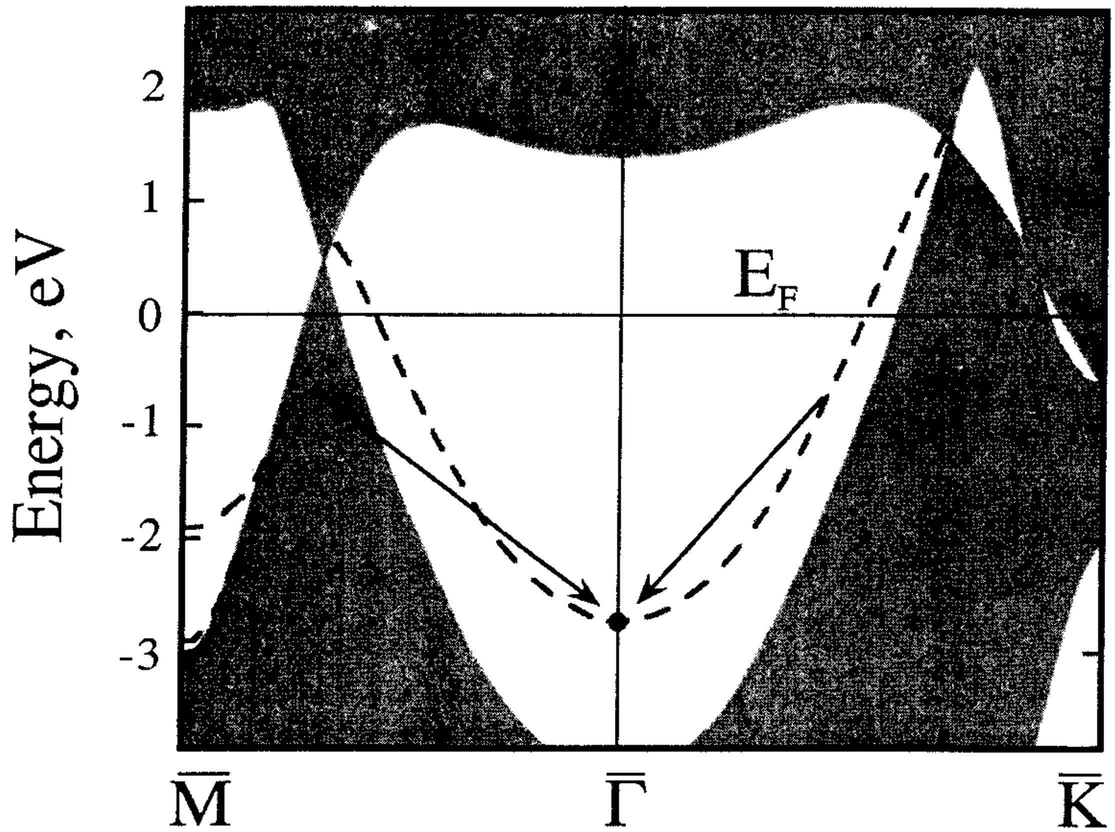


Linewidth of intrinsic surface state at $\bar{\Gamma}$ point



Γ (meV)	3D	Model potential
Cu	5.3	6
Be	92	40

Be(0001) Surface Band Structure



Be(0001)

Surface State Linewidth at $\bar{\Gamma}$ in meV

Comment	Γ_{total}	$\Gamma_{intraband}$	$\Gamma_{interband}$
1 dim. screening $m^*=1.49$ k-dependence of the penetration of the surface state	**280**	**240**	**40**
3 dim. screening 3 dim. wave function first principles	**265**	**225**	**40**

"First of all, image-potential states, because of their simplicity, provide an extremely useful model to study the interaction of excited surface electronic states with the underlying substrate directly in the time domain. This coupling in turn governs the cross sections and branching ratios of practically all electronically induced adsorbate reactions at metal surfaces.

(The lifetime of the excited state is the most important "unknown" in the Menzel-Gomer-Readhead model that is commonly used to describe electronically induced desorption and dissociation processes at surfaces).

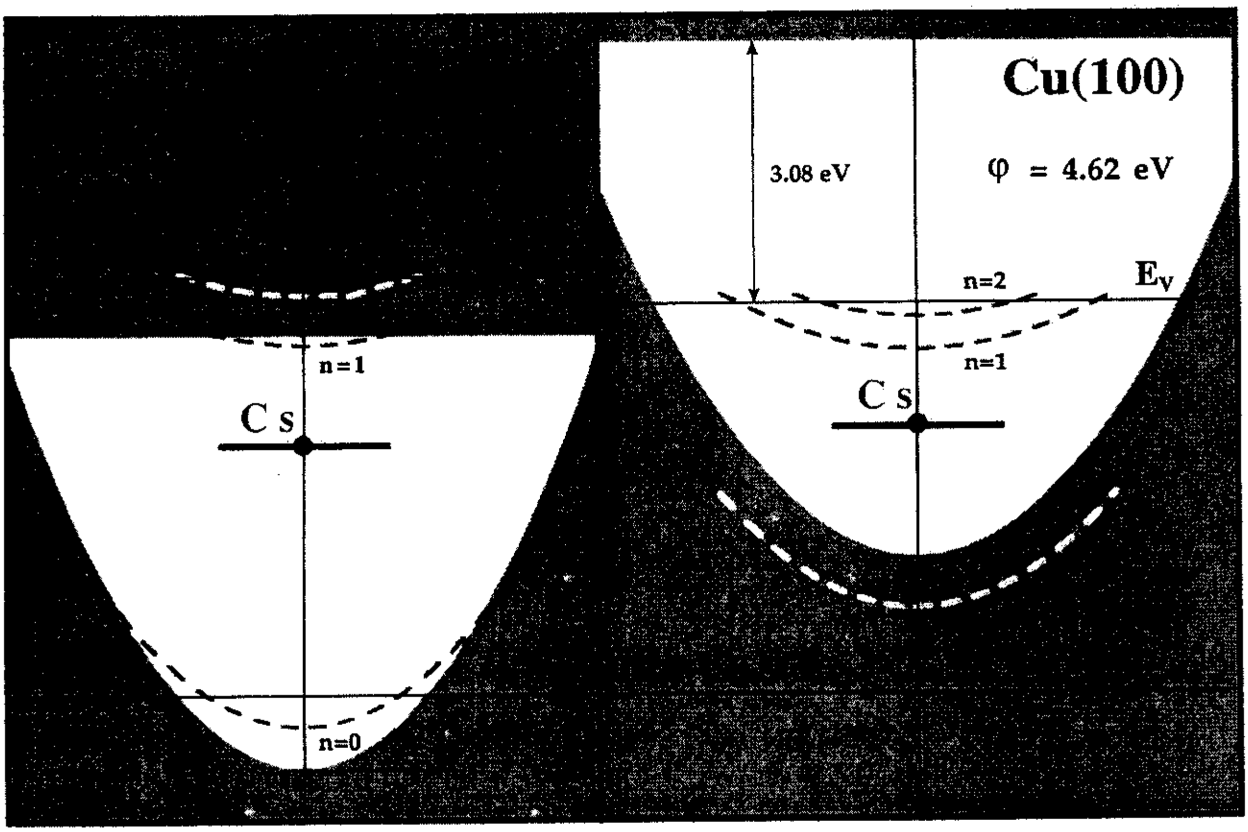
Second, there are numerous applications and extensions that come to mind..."

Ward Plummer on Science (Sept. 1997),
on the paper of **Höfer**
(same issue of Science).

IMAGE STATES LIFETIMES (fs)

		Theory	Experiment	
Cu(100)	n=1	38	40±6	U. Höfer *et al.* (1997)
	n=2	168	120±15	I.L. Shumay *et al.* (1998)
Cu(111)	n=1	17.5	18±5	M. Wolf *et al.* (1996)
	n=1		15±5	I.L. Shumay *et al.* (1998)
	n=1	23	22±3	E. Knoesel *et al.* (1998)
Resonance	n=2	28	-	
Ag(100)	n=1	38	55±5	I.L. Shumay *et al.* (1998)
	n=2	169	160±10	
	n=3	469	360±15	
Au(100)	n=1	22	-	
	n=2	93	-	
Pd(100)	n=1	11	-	
	n=2	56	-	
Pd(111)	n=1	22	25±4	A. Schäfer *et al.* (2000)
	n=2	89	-	
Ru(0001)	n=1	14	11^{+6}	W. Berthold *et al.* (2000)
	n=2	70	60	
Li(110)	n=1	18	-	
	n=2	44	-	

Cs/Cu(111) and Cs/Cu(100) Surface Band Structure



Linewidth (meV)

	Experiment		Theory	
	M.Bauer et al[1]	S.Ogawa et al[2]	Elastic[3]	Inelastic
(100)	110^{+220}_{-44}	130	112	20
(111)	44^{+29}_{-13}	13	10	17

[1]M.Bauer, S.Pawlik, and M.Aeschlimann, Phys. Rev. B60, 5016 (1999).

[2]S.Ogawa, H.Nagano, and H.Petek, Phys. Rev. Lett. 82, 1931 (1999).

[3]J.P.Gauyacq et al.

NONLINEAR CALCULATION OF RELAXATION RATES OF ELECTRONS AND HOLES IN A FREE ELECTRON GAS

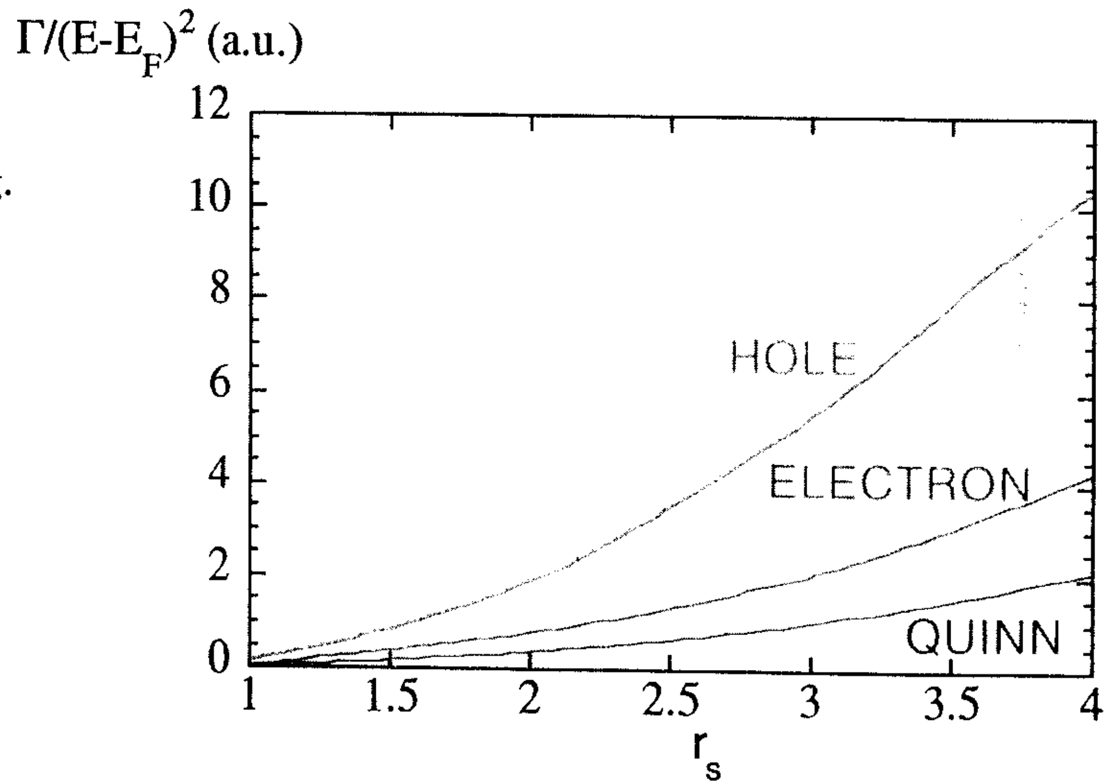
I. Nagy, I. Juaristi and P. M. Echenique (Submitted to PRB)

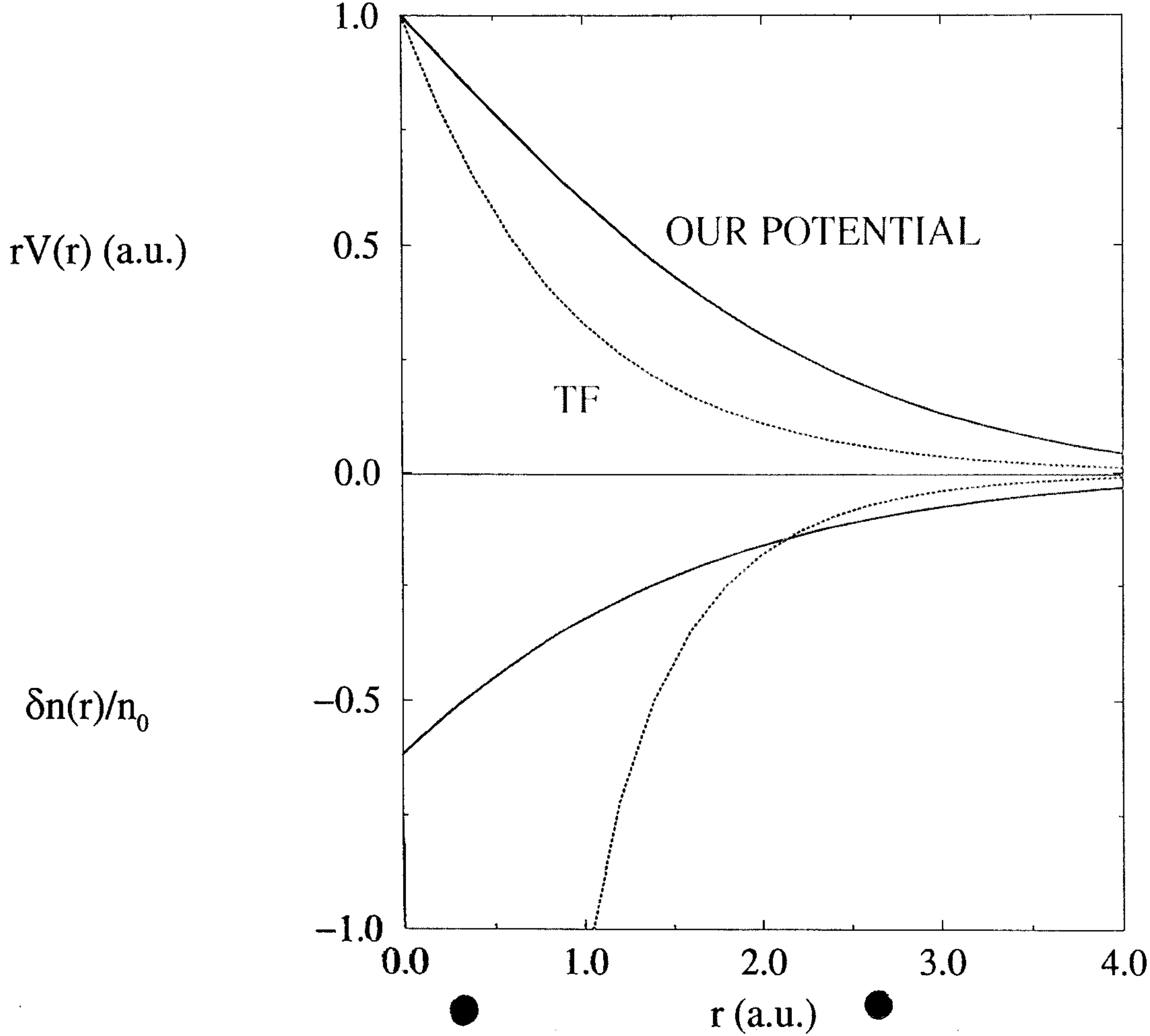
BASIC INGREDIENTS

- Pines -Nozieres: kinetic (binary) model for particle-particle scattering.

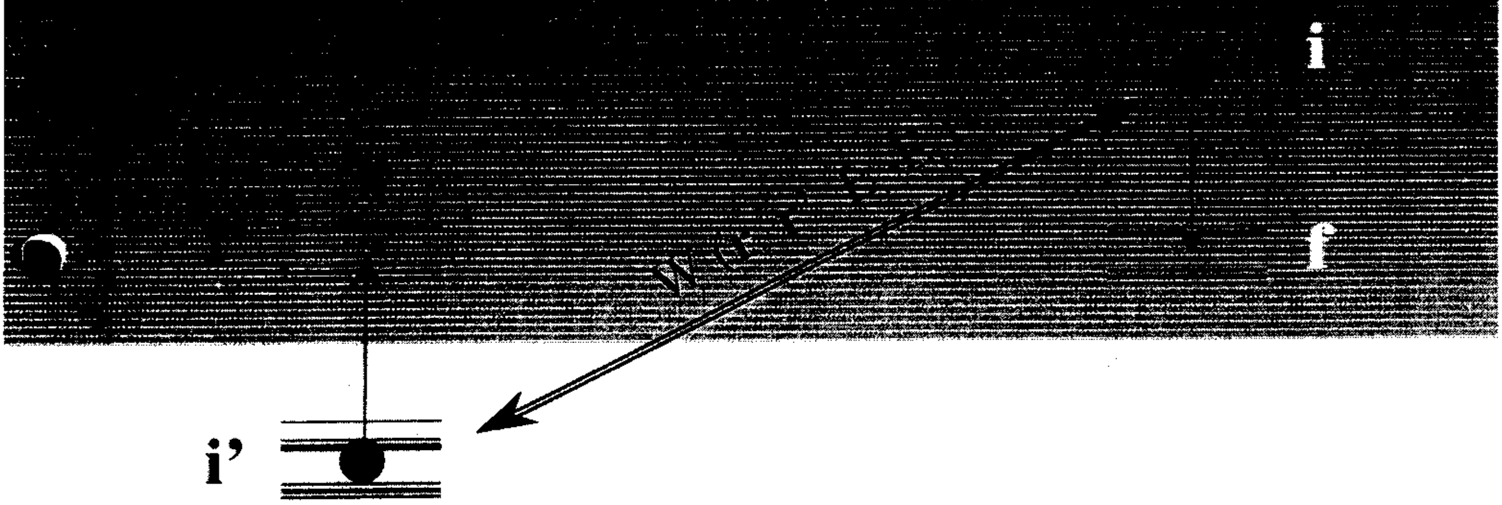
- Partial wave expansion for the scattering amplitudes (c. m. s).

- Construction of a model effective potential:
Proper normalization of the induced charge for moving ($v=v_F$) charges.




rV(r) (a.u.)
δn(r)/n0
OUR POTENTIAL
TF
1.0
0.5
0.0
−0.5
−1.0
0.0
1.0
2.0
3.0
4.0
r (a.u.)

In collaboration with...



- . Goldmann, Kassel, Germany
- . Balasubramanian, Lund, Sweden
- R. Berndt, Aachen, Germany
- U. Höfer, Marburg, Germany
- Th. Fauster, Erlangen, Germany