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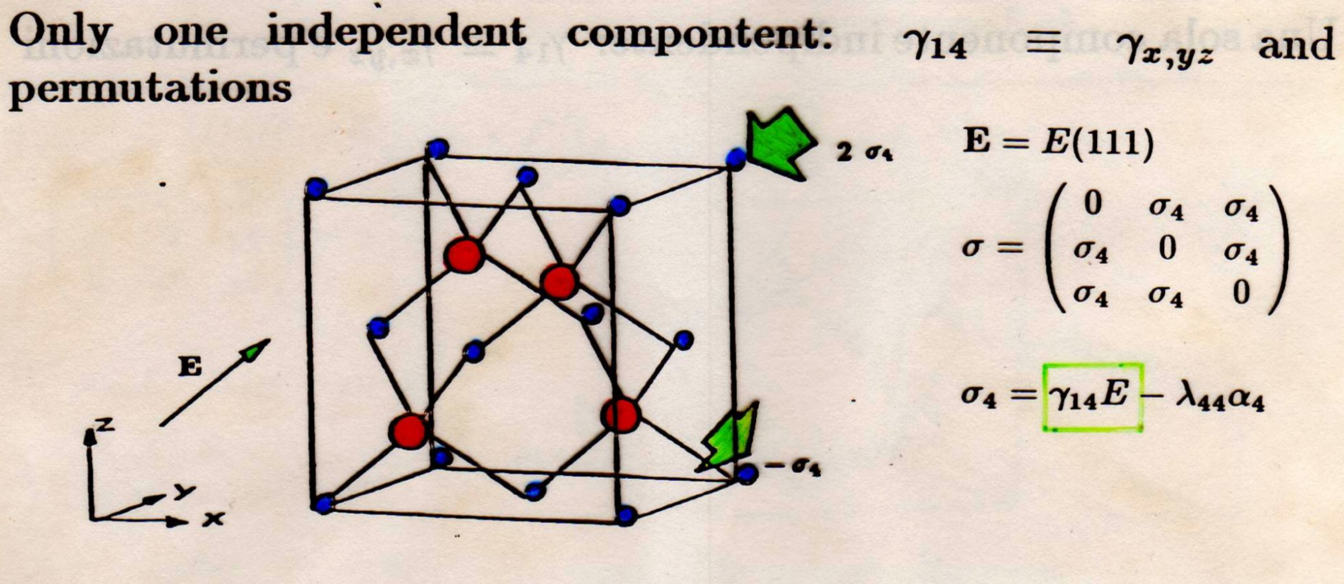
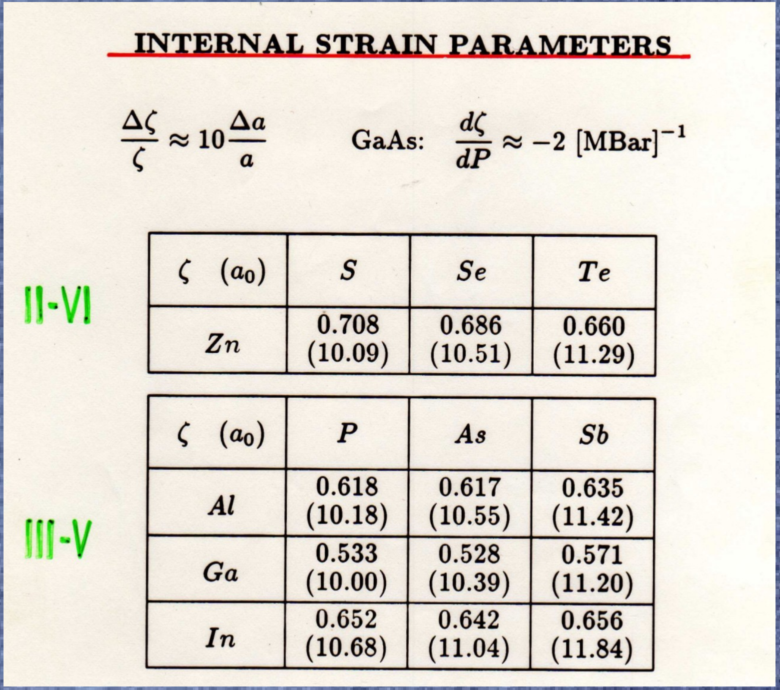


Only one independent compontent: $\gamma_{14} \equiv \gamma_{x,yz}$ and permutations

$$\mathbf{E} = E(111)$$

$$\sigma = \begin{pmatrix} 0 & \sigma_4 & \sigma_4 \\ \sigma_4 & 0 & \sigma_4 \\ \sigma_4 & \sigma_4 & 0 \end{pmatrix}$$

$$\sigma_4 = \boxed{\gamma_{14} E} - \lambda_{44}\alpha_4$$



INTERNAL STRAIN PARAMETERS

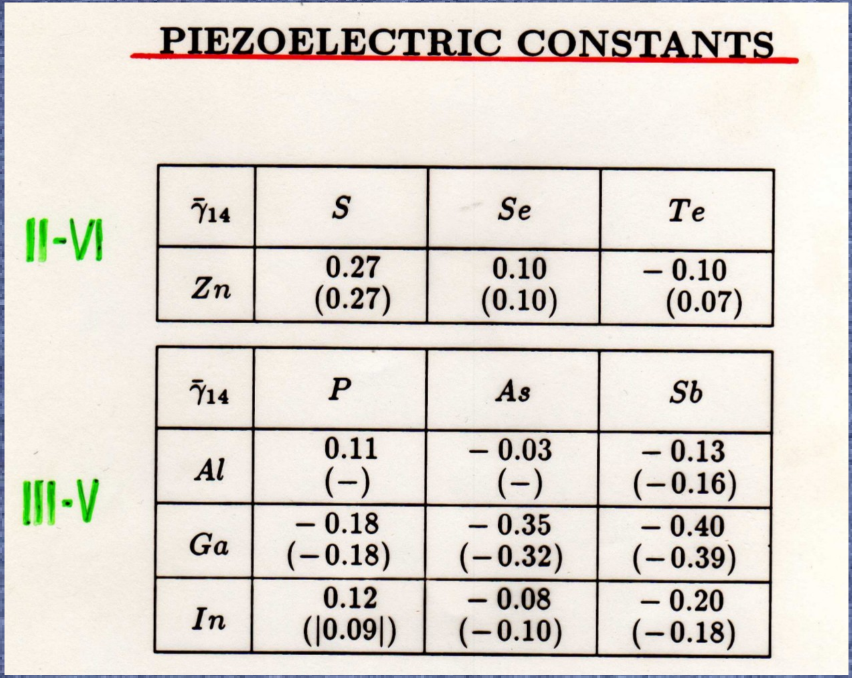
$$\frac{\Delta\zeta}{\zeta} \approx 10 \frac{\Delta a}{a} \qquad \text{GaAs:} \quad \frac{d\zeta}{dP} \approx -2\ [\text{MBar}]^{-1}$$

II-VI

ζ (a_0)	S	Se	Te
Zn	0.708 (10.09)	0.686 (10.51)	0.660 (11.29)

III-V

ζ (a_0)	P	As	Sb
Al	0.618 (10.18)	0.617 (10.55)	0.635 (11.42)
Ga	0.533 (10.00)	0.528 (10.39)	0.571 (11.20)
In	0.652 (10.68)	0.642 (11.04)	0.656 (11.84)



PIEZOELECTRIC CONSTANTS

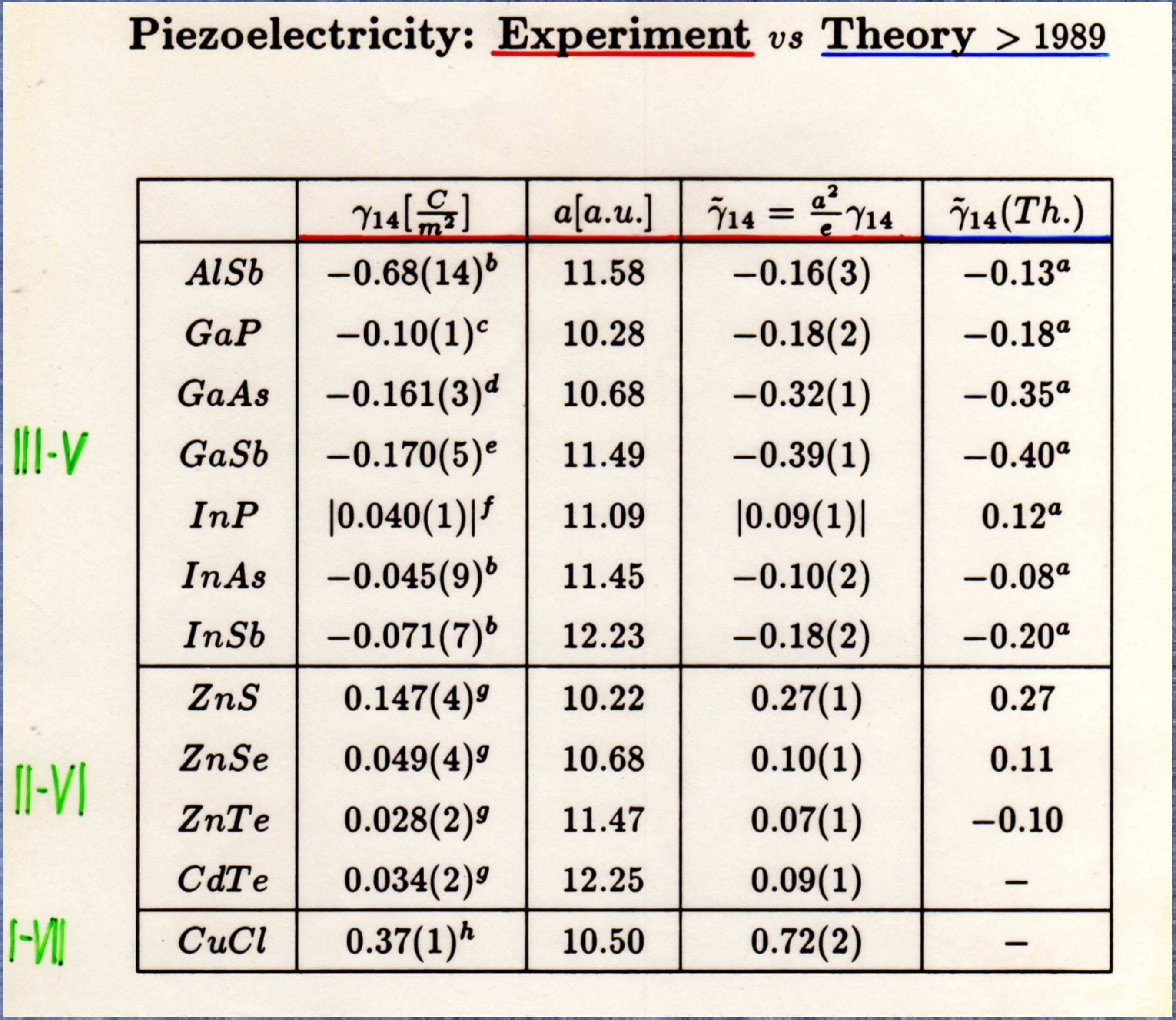
II-VI

$\bar{\gamma}_{14}$	S	Se	Te
Zn	0.27 (0.27)	0.10 (0.10)	− 0.10 (0.07)

III-V

$\bar{\gamma}_{14}$	P	As	Sb
Al	0.11 (−)	− 0.03 (−)	− 0.13 (− 0.16)
Ga	− 0.18 (− 0.18)	− 0.35 (− 0.32)	− 0.40 (− 0.39)
In	0.12 (|0.09|)	− 0.08 (− 0.10)	− 0.20 (− 0.18)

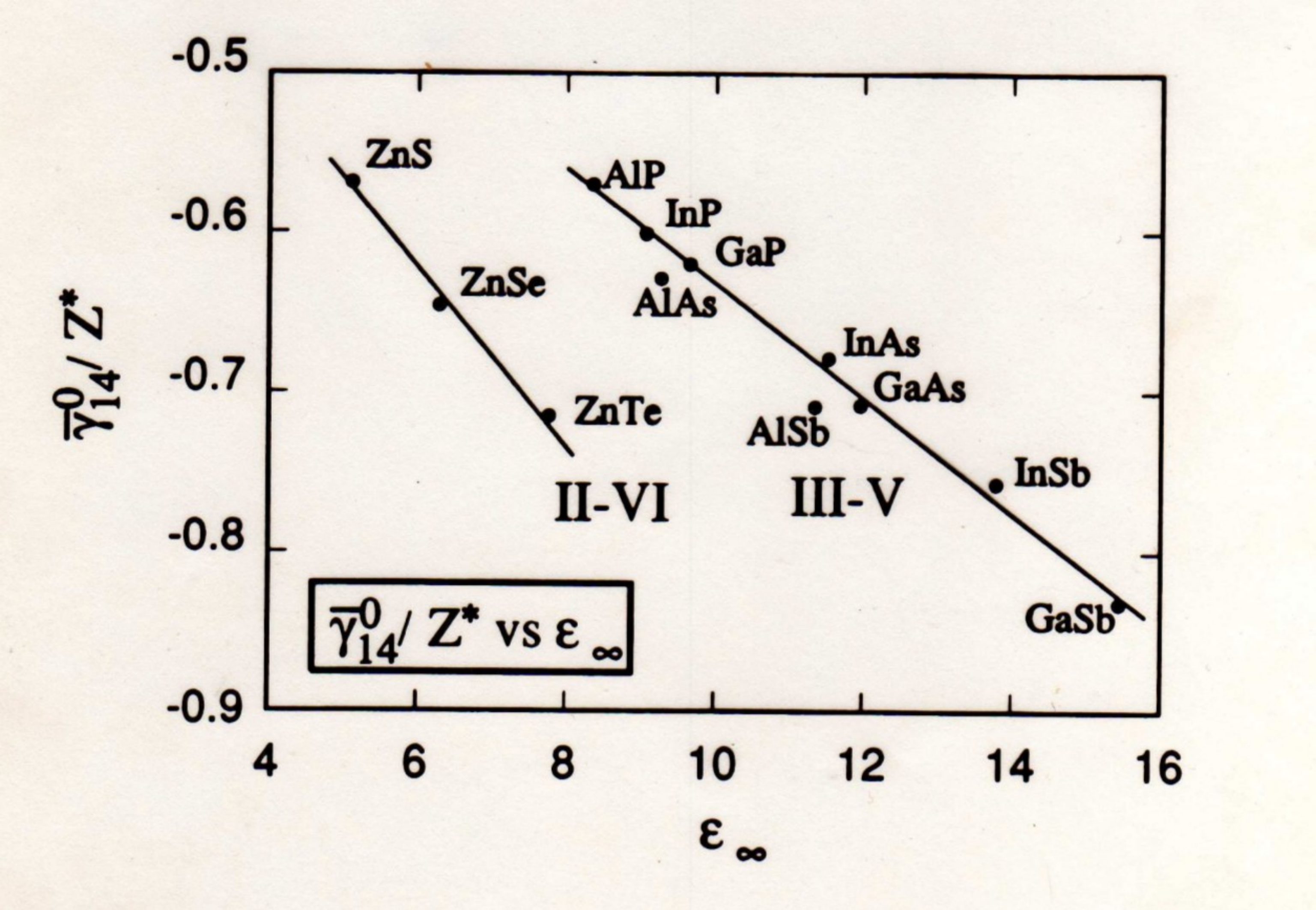
- **Piezoelctricity of III-V and II-VI semiconductors from Modern theory of Polarization.**



Piezoelectricity: Experiment *vs* **Theory** > 1989

		$\gamma_{14}[\frac{C}{m^2}]$	$a[a.u.]$	$\tilde{\gamma}_{14} = \frac{a^2}{e}\gamma_{14}$	$\tilde{\gamma}_{14}(Th.)$
III-V	$AlSb$	$-0.68(14)^b$	11.58	$-0.16(3)$	-0.13^a
	GaP	$-0.10(1)^c$	10.28	$-0.18(2)$	-0.18^a
	$GaAs$	$-0.161(3)^d$	10.68	$-0.32(1)$	-0.35^a
	$GaSb$	$-0.170(5)^e$	11.49	$-0.39(1)$	-0.40^a
	InP	$\|0.040(1)\|^f$	11.09	$\|0.09(1)\|$	0.12^a
	$InAs$	$-0.045(9)^b$	11.45	$-0.10(2)$	-0.08^a
	$InSb$	$-0.071(7)^b$	12.23	$-0.18(2)$	-0.20^a
II-VI	ZnS	$0.147(4)^g$	10.22	$0.27(1)$	0.27
	$ZnSe$	$0.049(4)^g$	10.68	$0.10(1)$	0.11
	$ZnTe$	$0.028(2)^g$	11.47	$0.07(1)$	-0.10
	$CdTe$	$0.034(2)^g$	12.25	$0.09(1)$	–
I-VII	$CuCl$	$0.37(1)^h$	10.50	$0.72(2)$	–

- **Piezoelctricity of III-V and II VI semiconductors from Modern theory of Polarization.**



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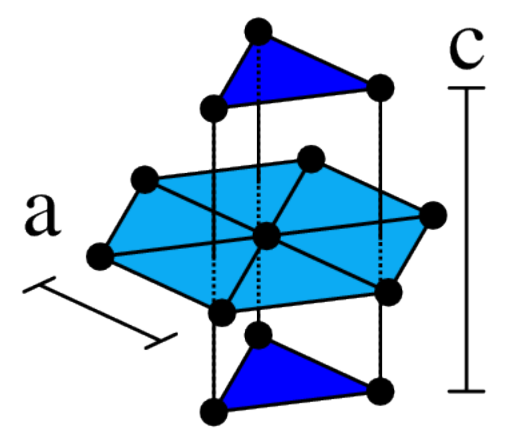
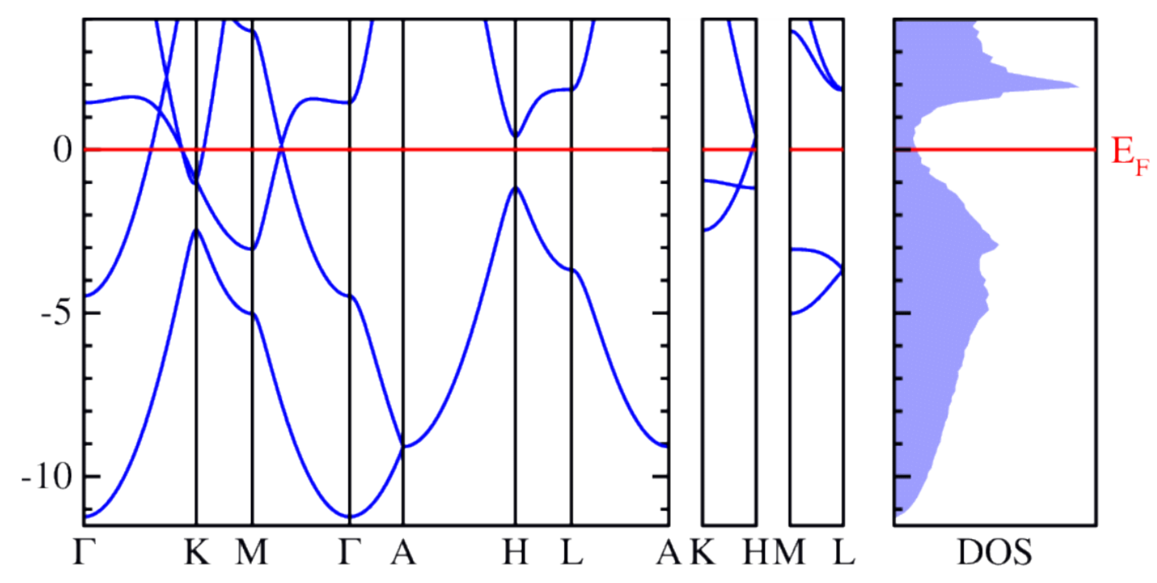
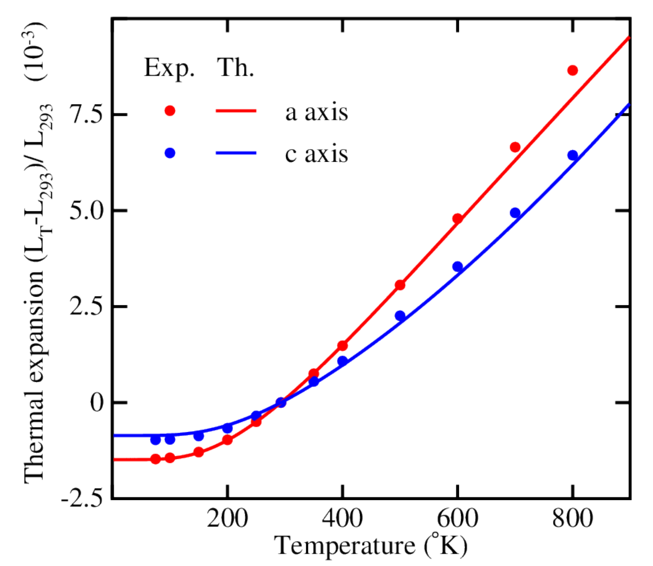
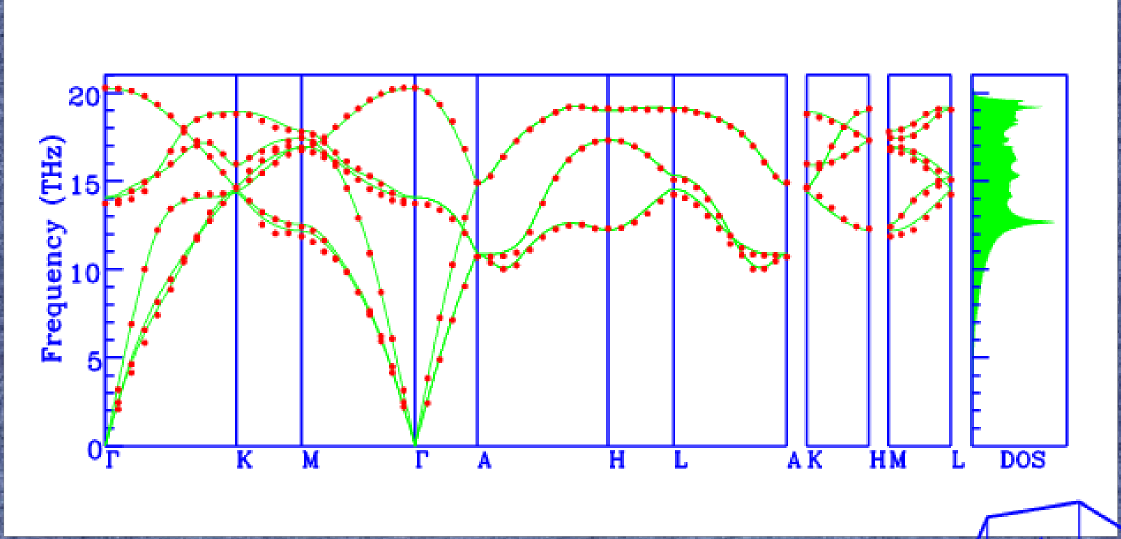
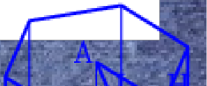
Be (0001) surface with vdW, surface relaxation, surface phonons, thermal expansion from QHA and from MD.



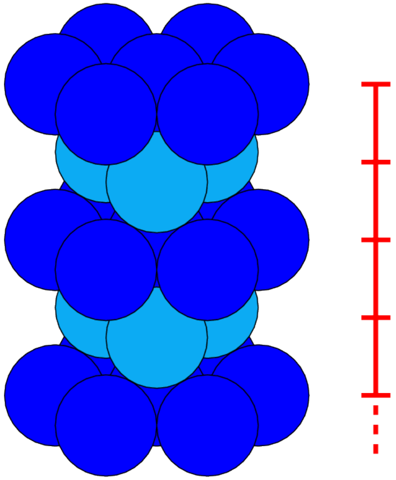






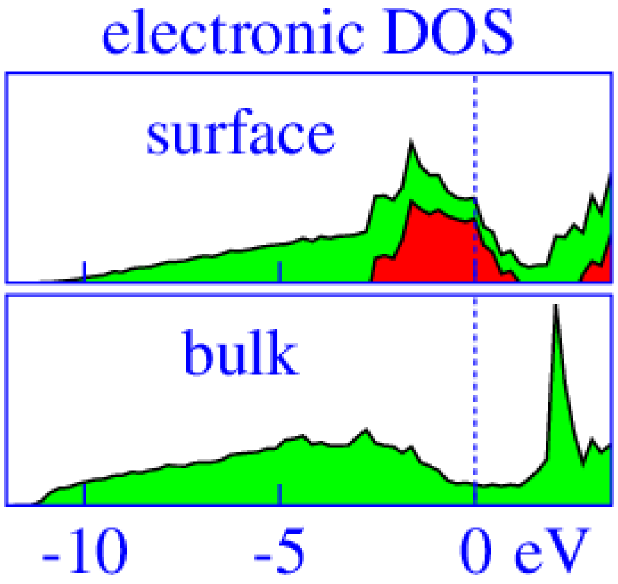


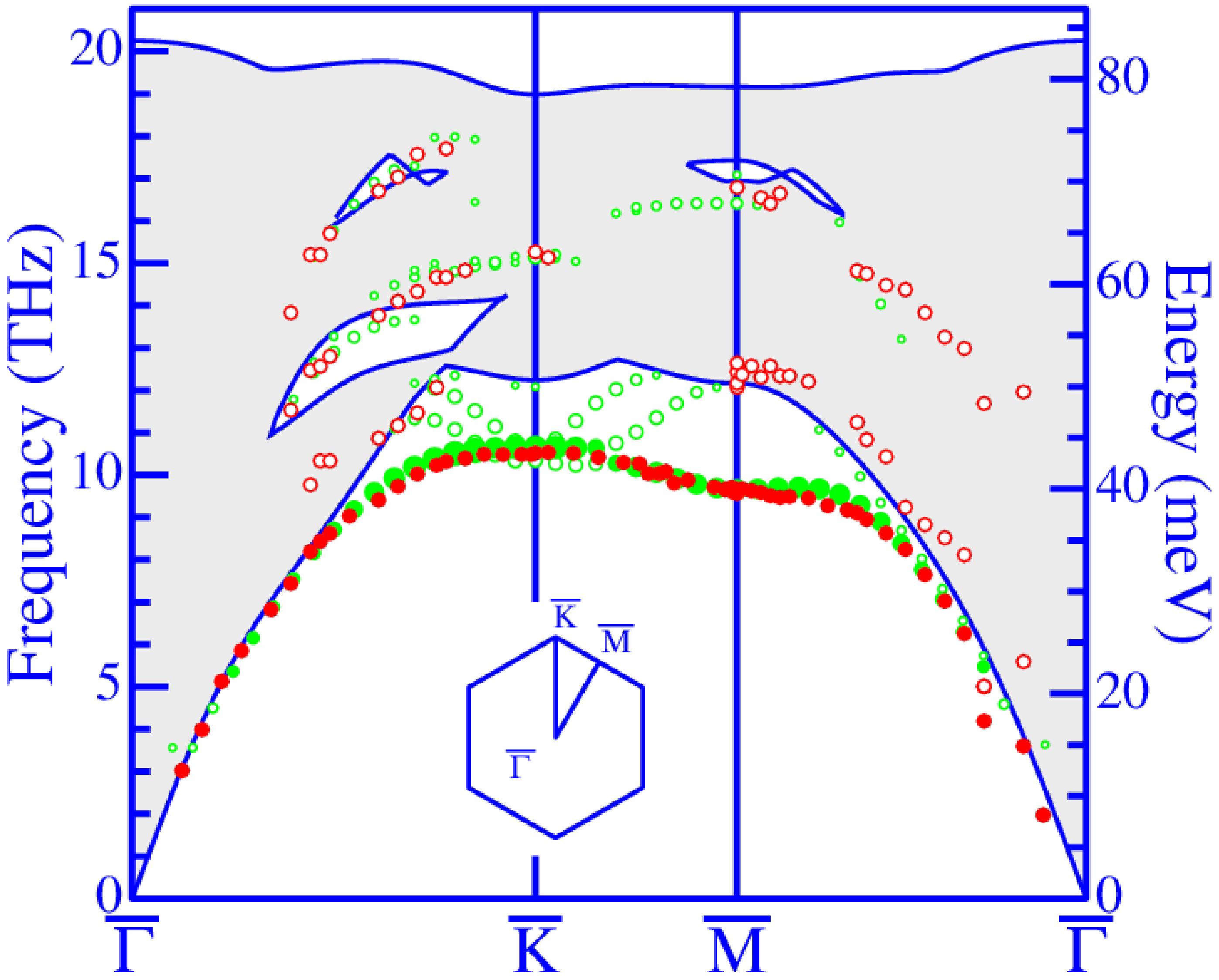
Be (0001) Surface



	300K	LDA	LDA
Δd_{12}	$+5.8\%$	$+2.7\%$	$+3.2\%$
Δd_{23}	-0.2%	$+1.2\%$	$+1.0\%$
Δd_{34}	$+0.2\%$	$+0.6\%$	$+0.4\%$

[300K] HL Davis et al. PRL 68, 2632 (1992)
[LDA] R Stumpf and PJ Feibelmann, PRB 51, 13748 (1995)
[LDA] M Lazzeri and SdG, Surf Sci 402–404, 715 (1998)





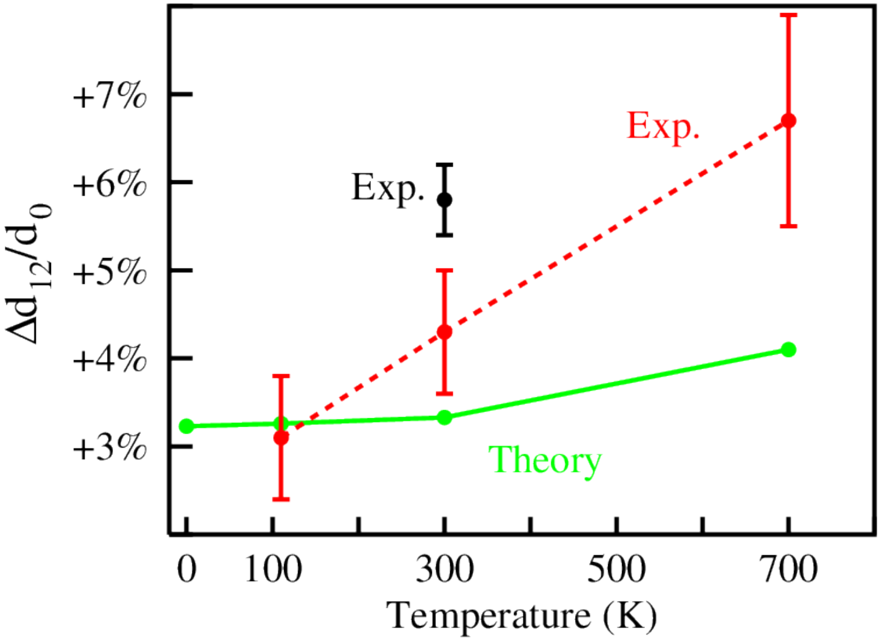
● Theory: more than 30% (z-polarized) on the top layer

○ Theory: more than 50% on the 3 topmost layers

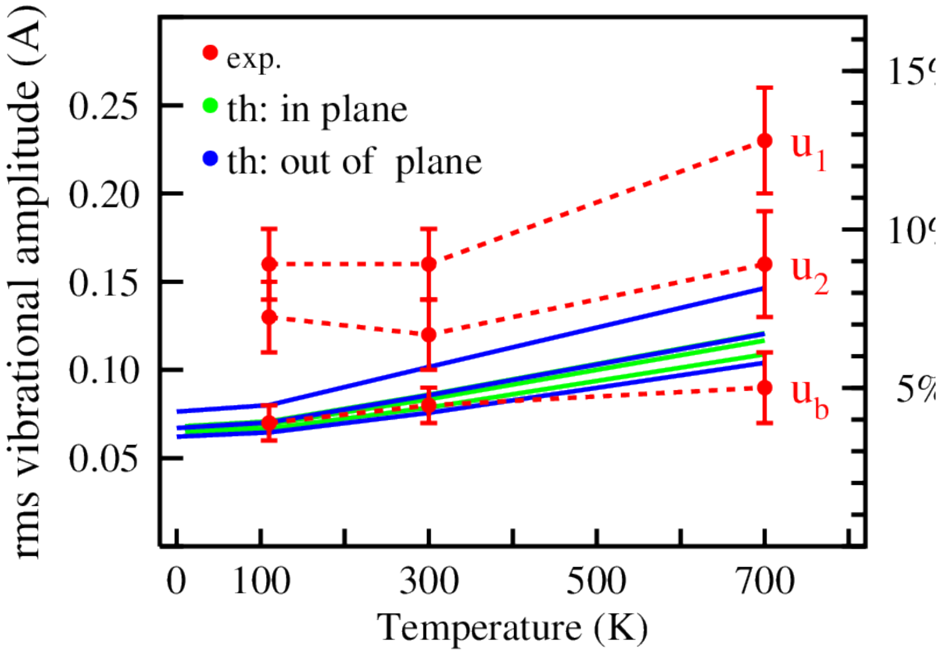
● EELS data: intense features (Rayleigh wave)

○ EELS data: weak features

Surface Thermal Expansion

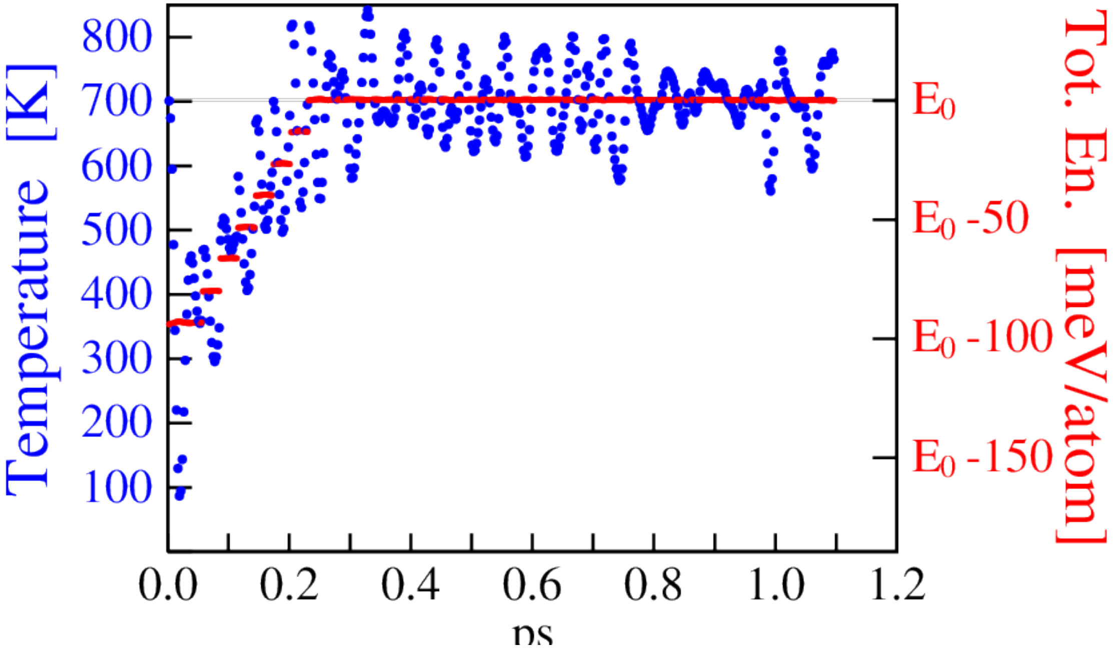


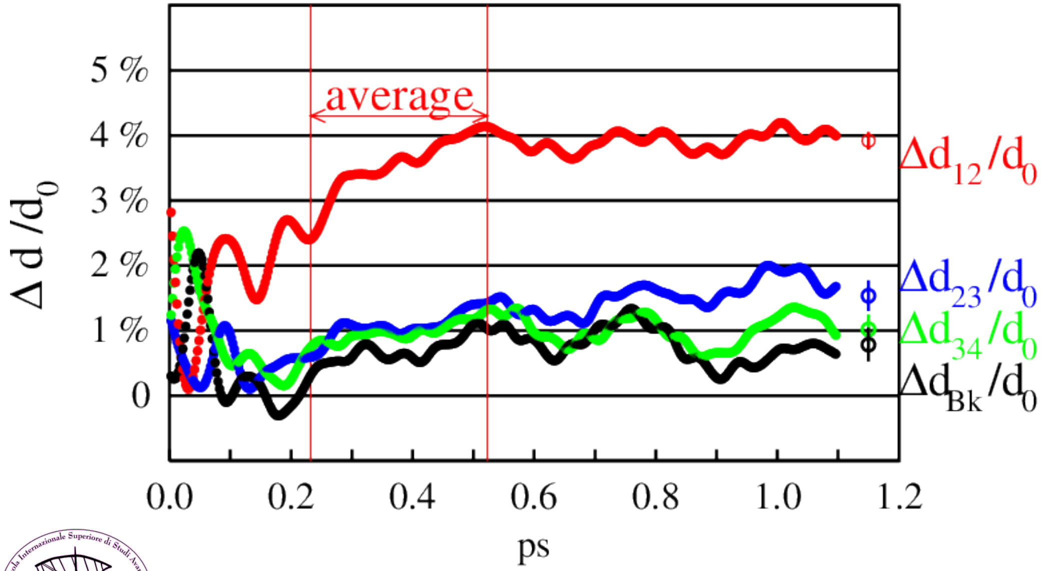
Vibrational Amplitude



Exp: LEED I-V HL Davis et al., PRL 68, 2632 (1992)
Exp: LEED I-V K Pohl et al., PRL 80, 2853 (1998)
Theory: M Lazzeri & SdG, PRL 81 2096 (1998)

First Principles Molecular Dynamics





700 K layer relaxation

	$FPMD$	QHA
Δd_{12}	$+3.9\%$	$+3.6\%$
Δd_{23}	$+1.6\%$	–
Δd_{34}	$+1.1\%$	–

700 K r.m.s. displ.

	$FPMD$	QHA
$u_1(\AA)$	0.16	0.14
$u_2(\AA)$	0.12	0.11
$u_3(\AA)$	0.11	0.10

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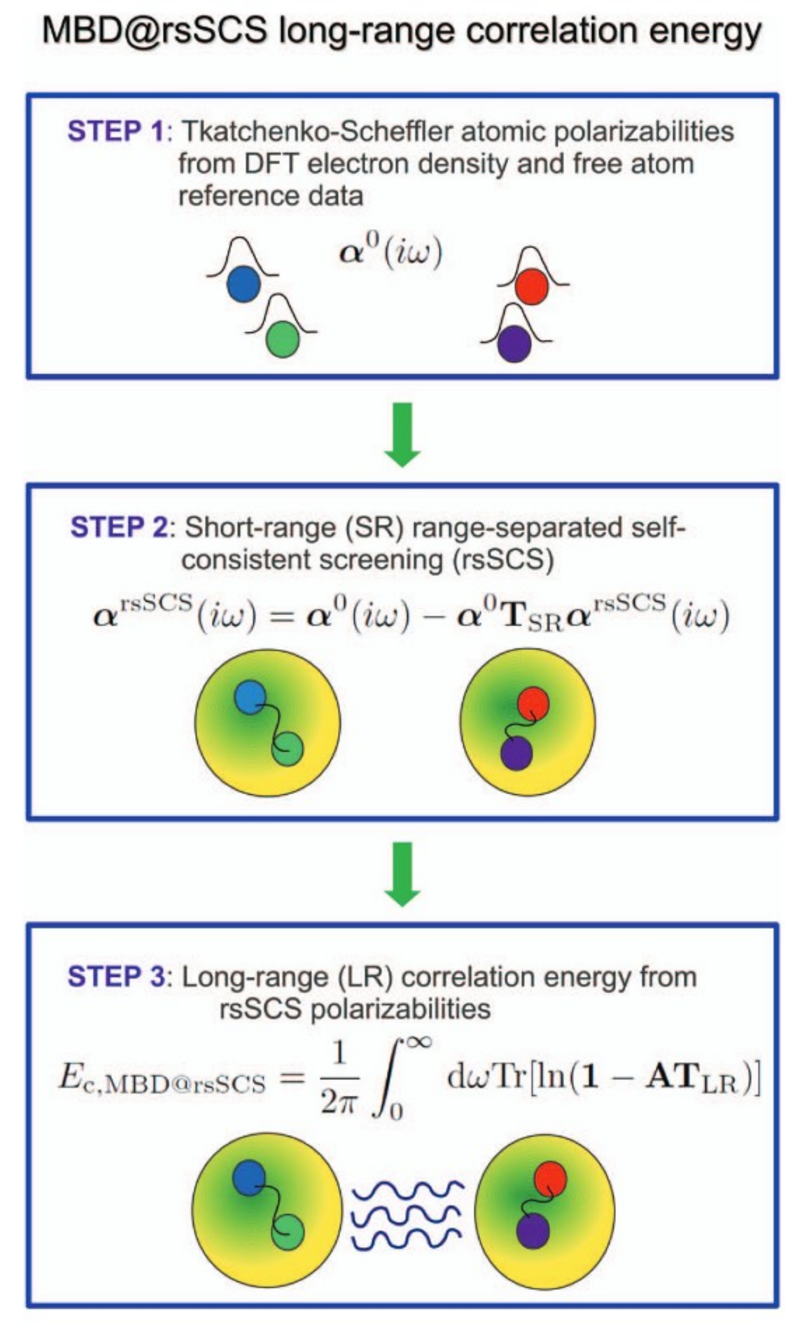

MBD@rsSCS long-range correlation energy

STEP 1: Tkatchenko-Scheffler atomic polarizabilities from DFT electron density and free atom reference data

$\boldsymbol{\alpha}^0(i\omega)$

STEP 2: Short-range (SR) range-separated self-consistent screening (rsSCS)

$$\boldsymbol{\alpha}^{\mathrm{rsSCS}}(i\omega) = \boldsymbol{\alpha}^0(i\omega) - \boldsymbol{\alpha}^0 \mathbf{T}_{\mathrm{SR}} \boldsymbol{\alpha}^{\mathrm{rsSCS}}(i\omega)$$

STEP 3: Long-range (LR) correlation energy from rsSCS polarizabilities

$$E_{\mathrm{c,MBD@rsSCS}} = \frac{1}{2\pi}\int_0^\infty d\omega \mathrm{Tr}[\ln(\mathbf{1} - \mathbf{AT}_{\mathrm{LR}})]$$

A Tkatchenko, RA Di Stasio, R Car, and M Scheffler, ``Accurate and efficient method for many-body van der waals interactions", PRL 108, 236402 (2012).

A Ambrosetti, AM Reilly, RA DiStasio, and A Tkatchenko, ``Long-range correlation energy calculated from coupled atomic response functions", JCP 140, 018A508 (2014).

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} \, \mathrm{Tr}\left\{\ln(1 - v\chi_0(i\omega)) + v\chi_0(i\omega)\right\},$$

$$\Phi^{VV10}(r,r') = -\frac{3e^4}{2m^2}\frac{1}{gg'(g+g')}$$

$$g = \omega_0(r)R^2 + k(r) \qquad k(r) = 3\pi b\left(\frac{n}{9\pi}\right)^{\frac{1}{6}}$$

$$\omega_0 = \sqrt{\omega_g^2 + \frac{\omega_p^2}{3}}, \quad \omega_g^2 = C\left(\frac{\hbar^2}{m^2}\right)\left|\frac{\nabla n}{n}\right|^4, \quad \omega_p^2 = \frac{4\pi n e^2}{m}$$

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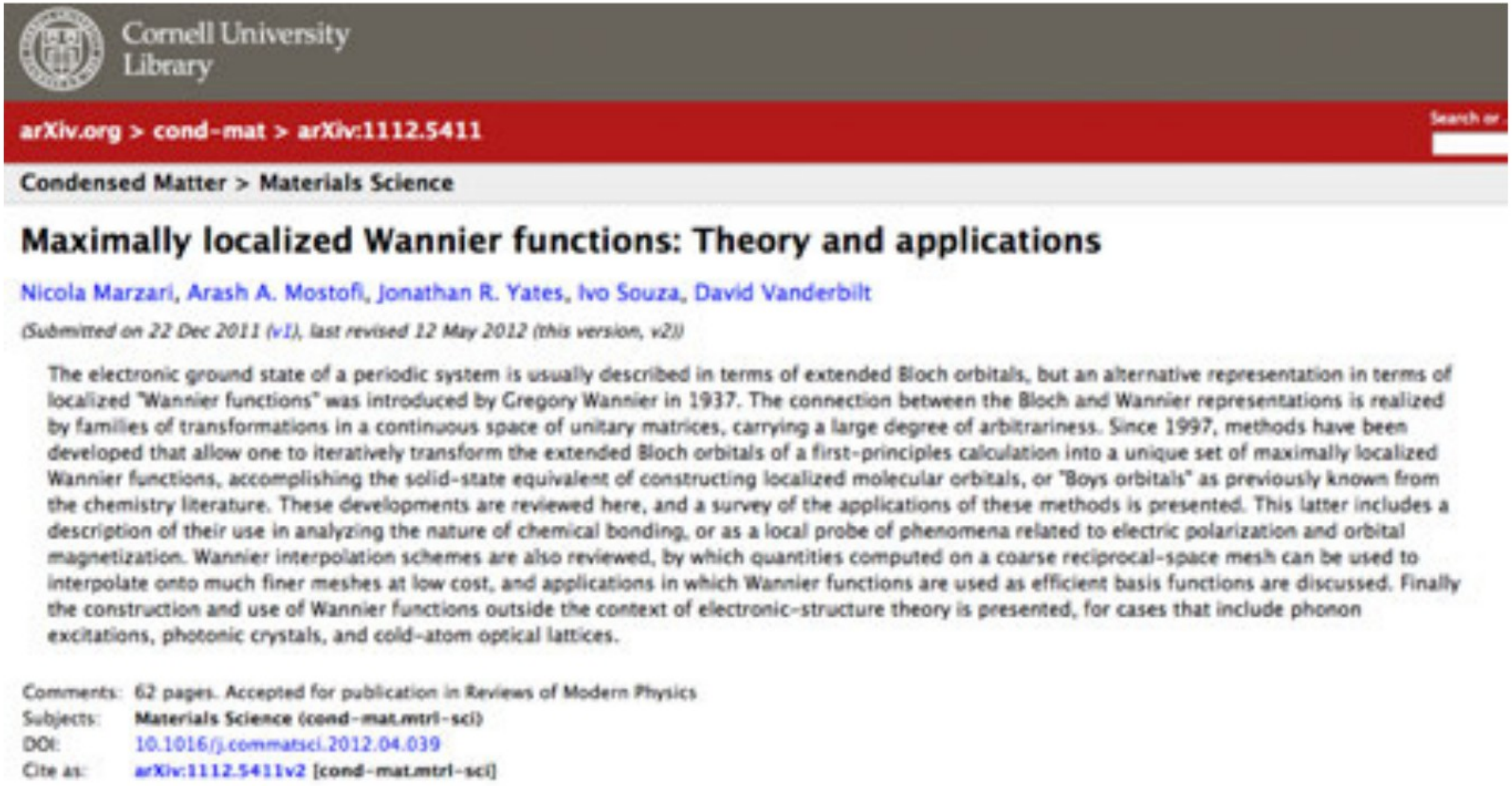
Reviews of Modern Physics (2012)



Maximally localized Wannier functions: Theory and applications

Nicola Marzari, Arash A. Mostofi, Jonathan R. Yates, Ivo Souza, David Vanderbilt

(Submitted on 22 Dec 2011 (v1), last revised 12 May 2012 (this version, v2))

The electronic ground state of a periodic system is usually described in terms of extended Bloch orbitals, but an alternative representation in terms of localized "Wannier functions" was introduced by Gregory Wannier in 1937. The connection between the Bloch and Wannier representations is realized by families of transformations in a continuous space of unitary matrices, carrying a large degree of arbitrariness. Since 1997, methods have been developed that allow one to iteratively transform the extended Bloch orbitals of a first-principles calculation into a unique set of maximally localized Wannier functions, accomplishing the solid-state equivalent of constructing localized molecular orbitals, or "Boys orbitals" as previously known from the chemistry literature. These developments are reviewed here, and a survey of the applications of these methods is presented. This latter includes a description of their use in analyzing the nature of chemical bonding, or as a local probe of phenomena related to electric polarization and orbital magnetization. Wannier interpolation schemes are also reviewed, by which quantities computed on a coarse reciprocal-space mesh can be used to interpolate onto much finer meshes at low cost, and applications in which Wannier functions are used as efficient basis functions are discussed. Finally the construction and use of Wannier functions outside the context of electronic-structure theory is presented, for cases that include phonon excitations, photonic crystals, and cold-atom optical lattices.

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Subjects:	Materials Science (cond-mat.mtrl-sci)
DOI:	10.1016/j.commatsci.2012.04.039
Cite as:	arXiv:1112.5411v2 [cond-mat.mtrl-sci]

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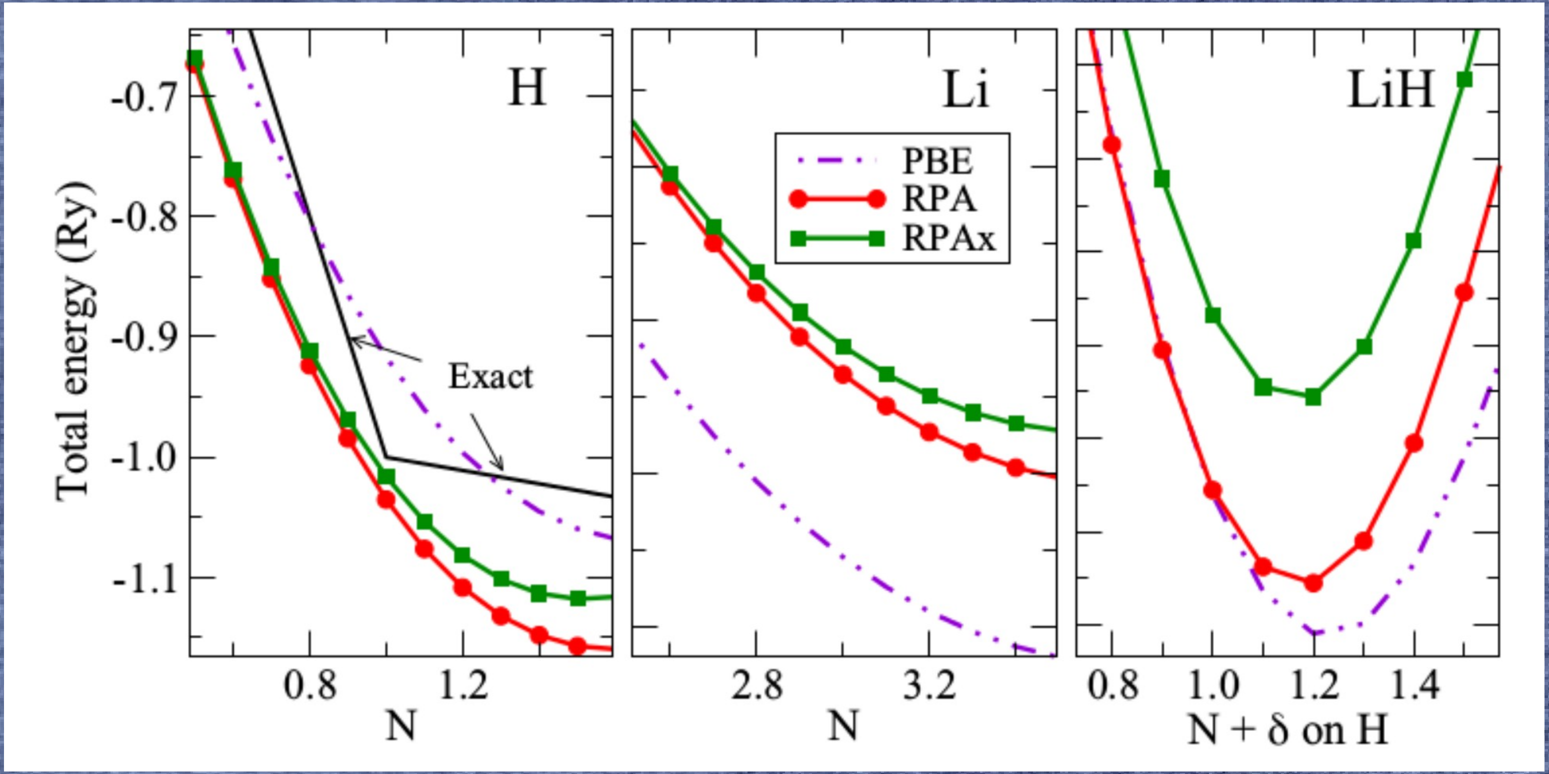

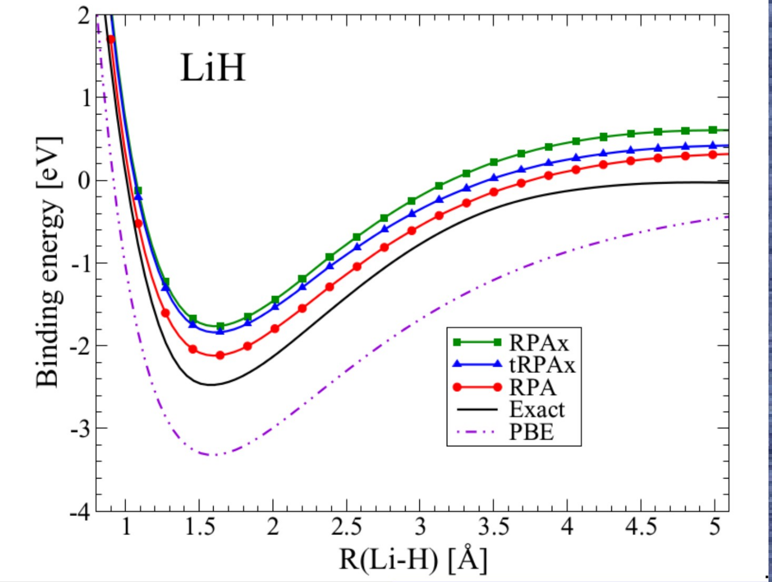

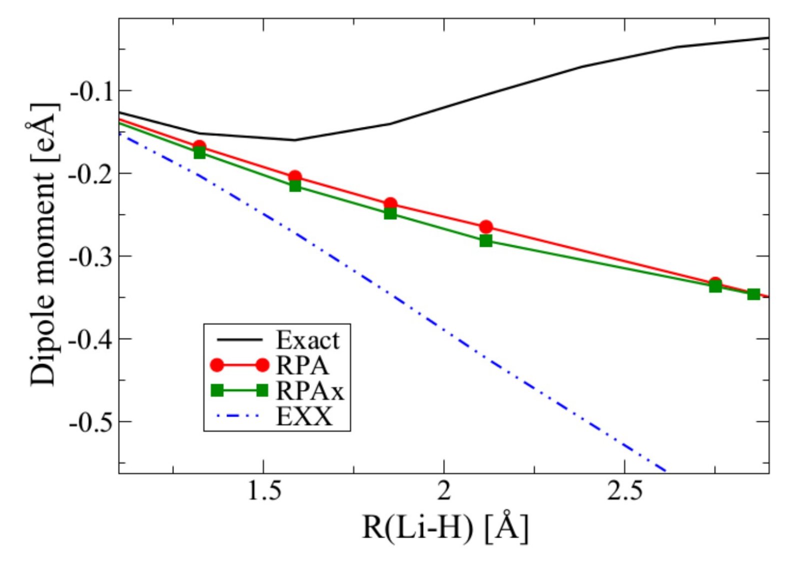

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Adiabatic Connection Fluctuation Dissipation

$$E_c[\rho] = -\frac{\hbar}{2\pi}\int_0^1 d\lambda \int_0^\infty du \, \mathrm{Tr} \; v_c[\chi_\lambda(iu) - \chi_0(iu)]$$

Dyson Equation for the response function

$$\chi_\lambda(iu) = \chi_0(iu) + \chi_0(iu)[\lambda v_c + f_{xc}^\lambda(iu)]\chi_\lambda(iu)$$

RPA: $f_{xc}^\lambda = 0$

RPA in QE.: V.H. Nguyen , SdG, PRB 79, 165406 (2009).
Scf RPA: N.L. Nguyen, N. Colonna, SdG, PRB 90, 045138 (2014).

OK for vdW interaction, overestimates correlation energy in absolute terms

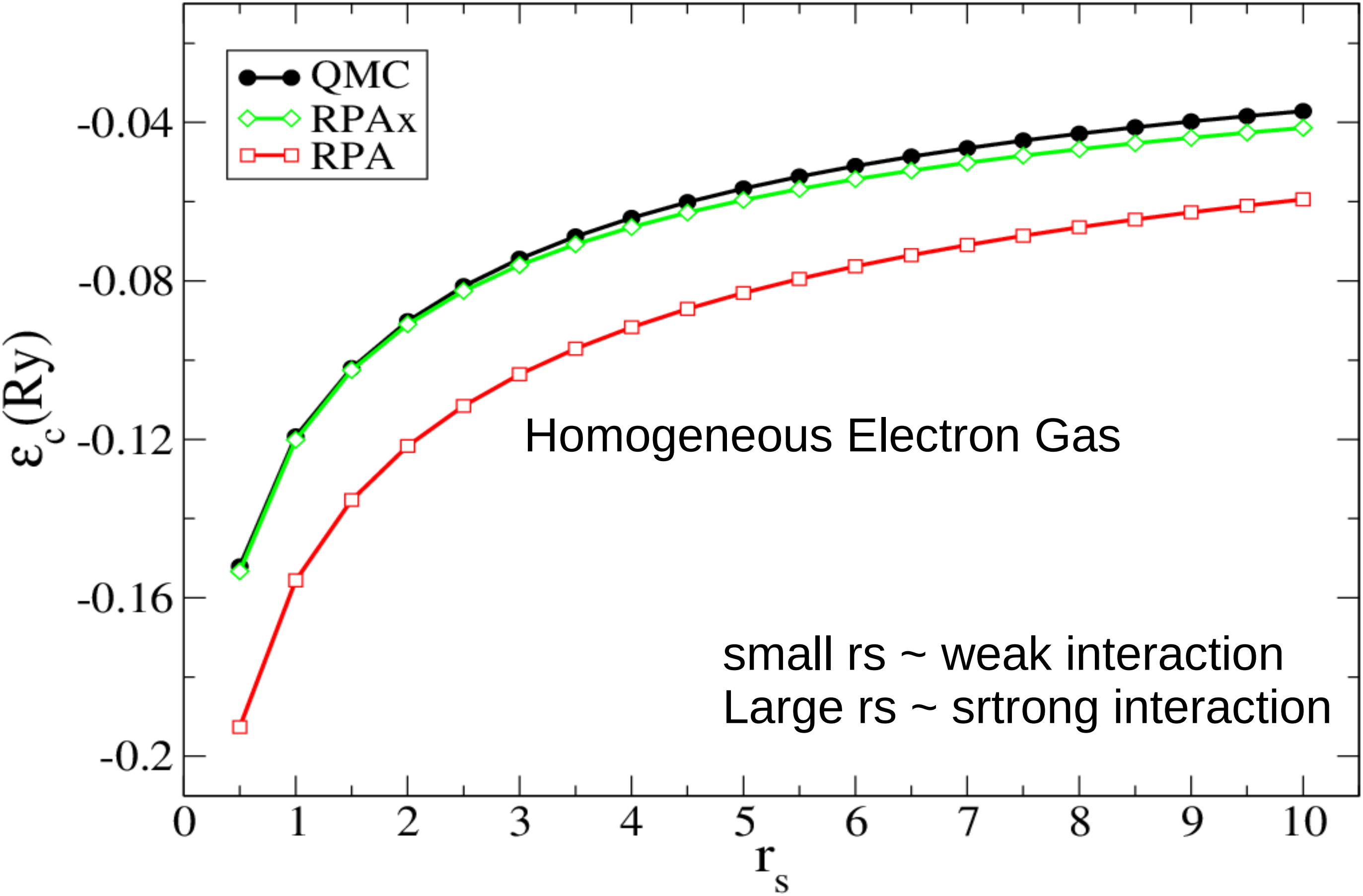
RPAx: $f_{xc}^\lambda = \lambda f_x$ RPAx in QE.: N. Colonna,M. Hellgren, SdG, PRB 90, 125150 (2014).

Much more accurate correlation energy, displays instabilities at low density
ScfRPAx still to be implemented.

- **Advanced xc functionals from ACFD formalism**

RPA: OK for vdW interaction but overestimates correlation energy

RPAx: much better energy, but displays instabilities at low density



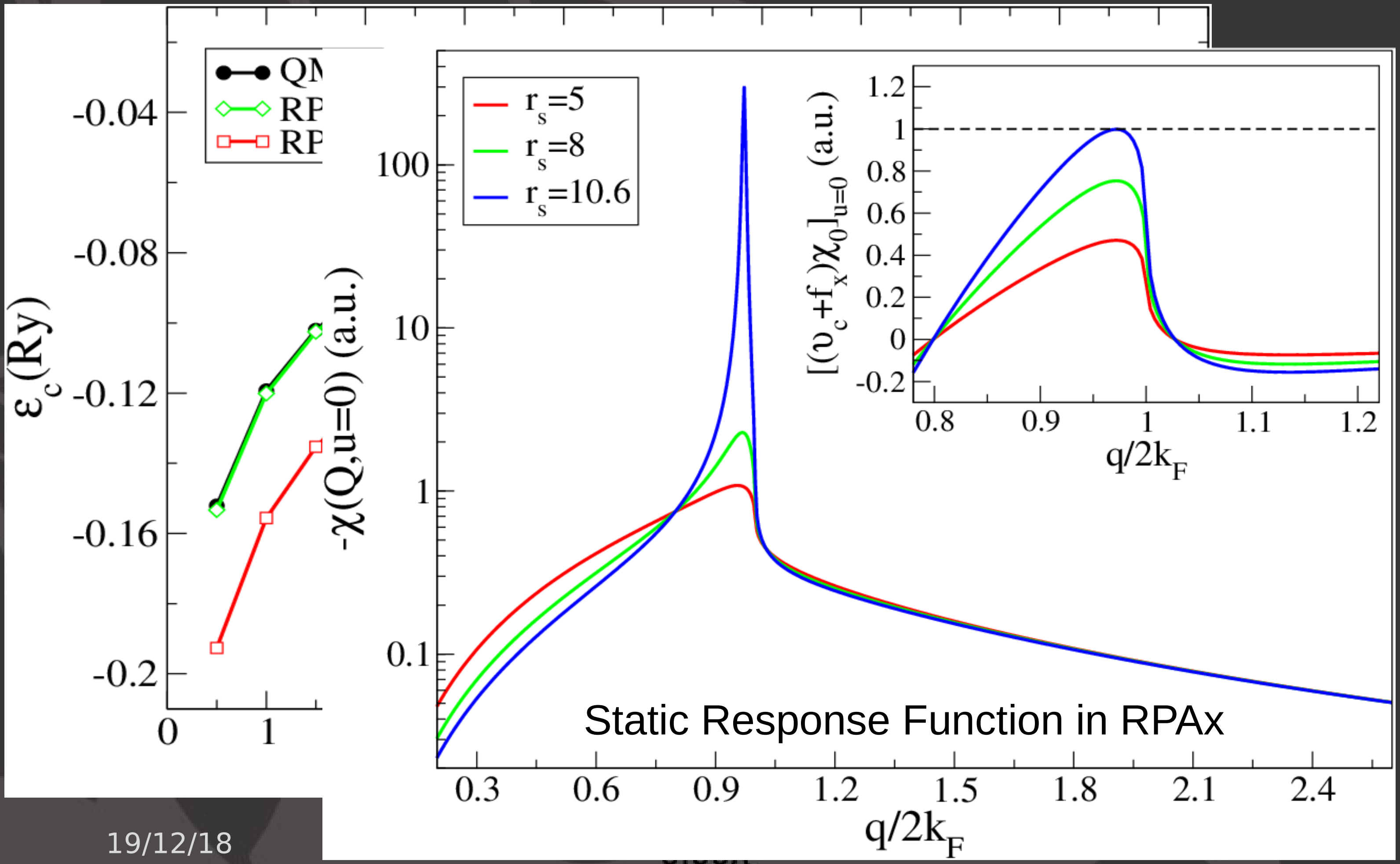
Homogeneous Electron Gas

small rs ~ weak interaction
Large rs ~ srtrong interaction

- # Advanced xc functionals from ACFD formalism

RPA: OK for vdW interaction but overestimates correlation energy

RPAx: much better energy, but displays instabilities at low density



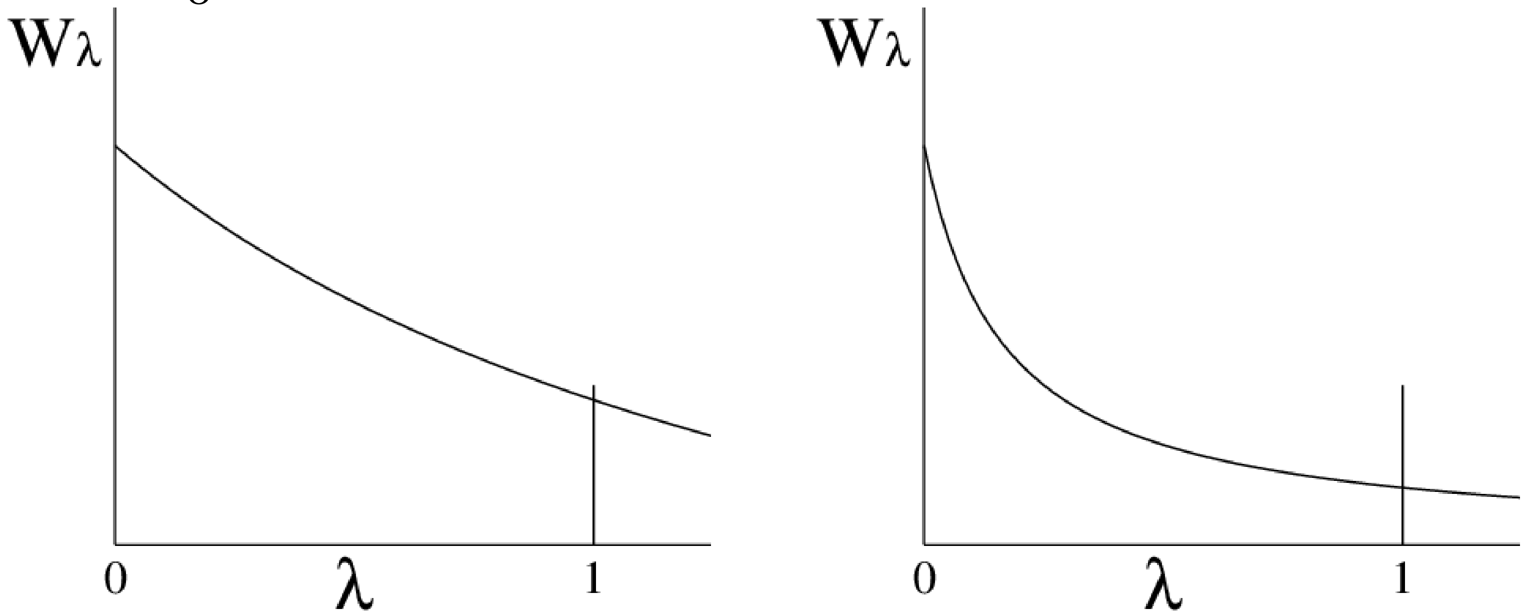
Static Response Function in RPAx

Interaction-Strength Interpolation

Compute accurate correlation energies interpolating between the exact results from the weak interaction limit (Exact exchange + GL2 2nd order Goerling-Levy PT) and some estimates in the strong interaction limit: PC (Point charge plus Continuum model)

M Seidl, JP Perdew & S Kurth, *PRL* **84**, 5070 (2000)

$$E_{xc}[\rho] = \int_0^1 d\lambda W_\lambda[\rho] \qquad W_\lambda[\rho] = \langle \Psi_\lambda[\rho]|V_{ee}|\Psi_\lambda[\rho]\rangle - U[\rho]$$



$$W_\lambda[\rho] = E_x[\rho] + 2E_c^{GL2}[\rho]\lambda + \ldots, \qquad \lambda \sim 0$$

$$W_\lambda[\rho] = W_\infty[\rho] + \frac{W'_\infty[\rho]}{\sqrt{\lambda}} + \ldots, \qquad \lambda \longrightarrow \infty$$

Interaction-Strength Interpolation

- The Taylor expansion of the ISI interpolation formula has a finite convergence radius

$$\alpha_c[\rho] = \frac{1}{Y[\rho]} = \frac{(E_x - W_\infty)^4}{16(E_c^{GL2} W'_\infty)^2}$$

that can give a feeling of the convergence properties of the, unknown, *“real”* expansion

- Beyond its conv. radius the series is highly unstable and its integral eventually diverges ...
- …even tho the interpolation itself is integrated without problems !

- *Many molecules in the previous slide have conv. radii << 1 !*

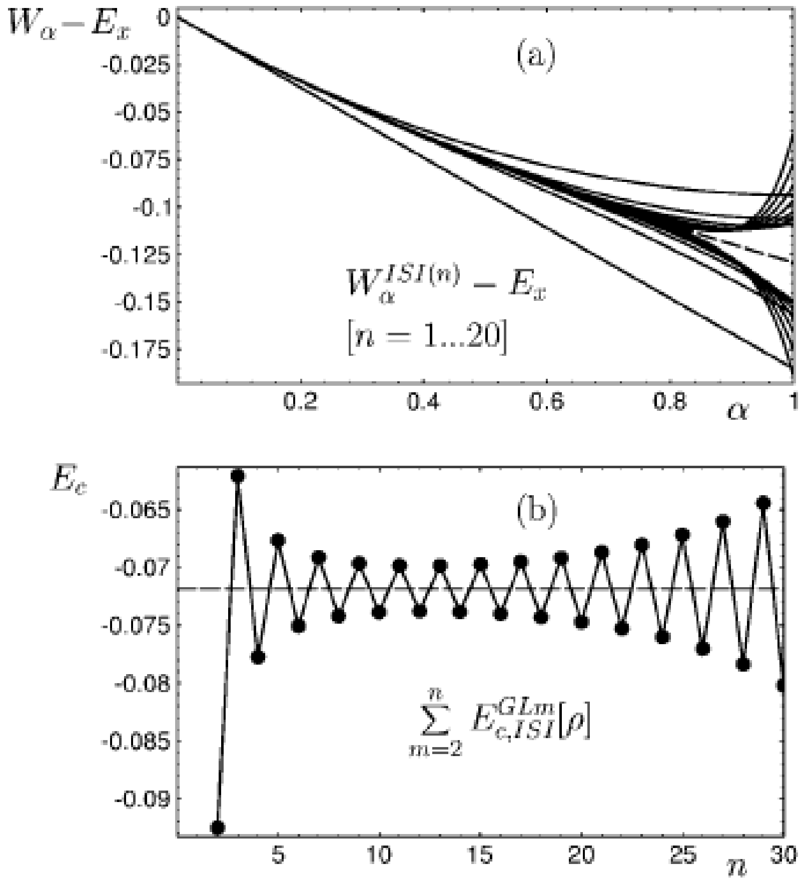
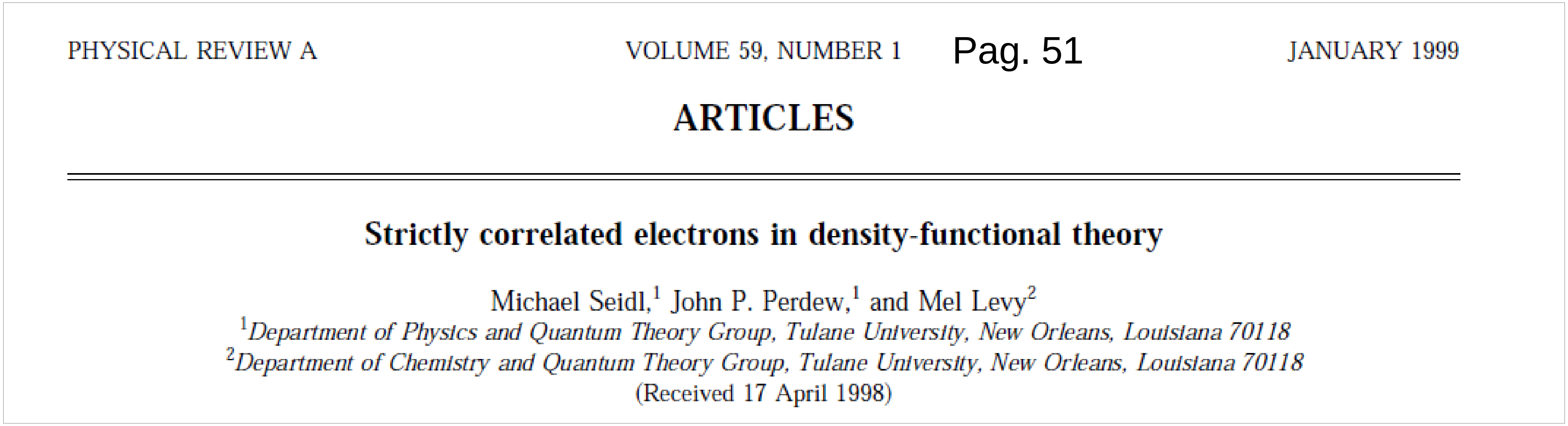


FIG. 1. (a) The model integrand $W_\alpha^{\rm ISI}$ [Eq. (9)] in arbitrary units for a system with $E_x - W_\infty = 1.0$, $E_c^{\rm GL2} = -0.0925$, and $W'_\infty = 3.0$ (dashed curve), and its truncated Taylor expansions of orders $n = 1$–20 (solid curves). The radius of convergence is $\alpha_c = 0.812$. (b) The corresponding integrated correlation energies $\sum_{m=2}^{n} E_{c,\rm ISI}^{{\rm GL}m}[\rho] = \int_0^1 d\alpha\, W_\alpha^{{\rm ISI}(n)}$ in nth order Görling-Levy perturbation theory (full circles) oscillate around $E_c^{\rm ISI}[\rho]$ (horizontal dashed line) and eventually diverge. (An accurate truncation of the series would include only half of the smallest term, $m = 13$, and all of the lower-order terms.)



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ARTICLES

Strictly correlated electrons in density-functional theory

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$$W_\alpha[\rho] = \langle \Psi_\alpha[\rho] | V_{ee} | \Psi_\alpha[\rho] \rangle - U[\rho]$$

Properties:

$$W_\alpha[\rho] = \alpha W_1[\rho_{1/\alpha}], \quad \rho_\lambda(r) = \lambda^3 \rho(\lambda r)$$

$$W'_\alpha[\rho] = \frac{dW_\alpha}{d\alpha}[\rho] < 0 \quad (\alpha \geq 0)$$

$$W_0[\rho] = E_x[\rho], \quad W'_0 = 2E_c^{GL2}$$

$$W_\infty[\rho] = \lim_{\alpha \longrightarrow \infty} W_\alpha[\rho] \quad (\text{finite} > -U[\rho])$$

A simple model $$W_\alpha^{mod}[\rho] = W_\infty + \frac{W_0 - W_\infty}{\sqrt{1 + 2X\alpha}}, \quad X = \frac{W'_0}{W_\infty - W_0}$$

Interaction-Strength Interpolation

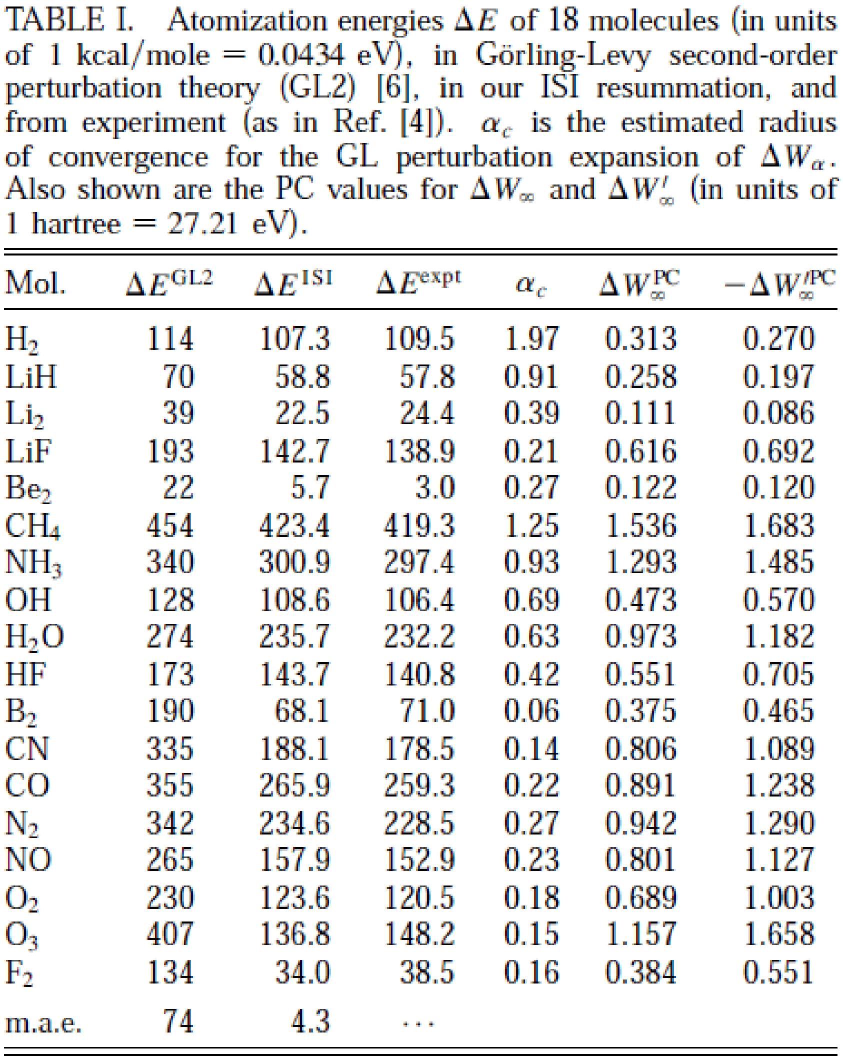

TABLE I. Atomization energies ΔE of 18 molecules (in units of 1 kcal/mole = 0.0434 eV), in Görling-Levy second-order perturbation theory (GL2) [6], in our ISI resummation, and from experiment (as in Ref. [4]). α_c is the estimated radius of convergence for the GL perturbation expansion of ΔW_α. Also shown are the PC values for ΔW_∞ and $\Delta W'_\infty$ (in units of 1 hartree = 27.21 eV).

Mol.	ΔE^{GL2}	ΔE^{ISI}	ΔE^{expt}	α_c	$\Delta W_\infty^{\mathrm{PC}}$	$-\Delta W_\infty^{\prime\mathrm{PC}}$
H_2	114	107.3	109.5	1.97	0.313	0.270
LiH	70	58.8	57.8	0.91	0.258	0.197
Li_2	39	22.5	24.4	0.39	0.111	0.086
LiF	193	142.7	138.9	0.21	0.616	0.692
Be_2	22	5.7	3.0	0.27	0.122	0.120
CH_4	454	423.4	419.3	1.25	1.536	1.683
NH_3	340	300.9	297.4	0.93	1.293	1.485
OH	128	108.6	106.4	0.69	0.473	0.570
H_2O	274	235.7	232.2	0.63	0.973	1.182
HF	173	143.7	140.8	0.42	0.551	0.705
B_2	190	68.1	71.0	0.06	0.375	0.465
CN	335	188.1	178.5	0.14	0.806	1.089
CO	355	265.9	259.3	0.22	0.891	1.238
N_2	342	234.6	228.5	0.27	0.942	1.290
NO	265	157.9	152.9	0.23	0.801	1.127
O_2	230	123.6	120.5	0.18	0.689	1.003
O_3	407	136.8	148.2	0.15	1.157	1.658
F_2	134	34.0	38.5	0.16	0.384	0.551
m.a.e.	74	4.3	⋯			

- Great improvement w.r.t results from PT
- However...
-
- the PT energies are not really computed but the energy differences are take from Ref 6 and the interpolation is applied to them.
-
- Size consistency would not be insured by the procedure applied to the individual terms.
-
- *In order to achieve size consistency*
- *a “local” version of the method is*
- *needed*

[6] Enrzerhof CPL **263,** 499 (1996)