

Excited-state properties from time-dependent density functional theory

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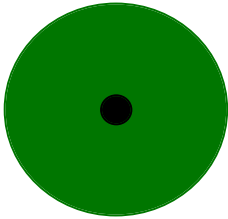
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TIME-DEPENDENT SYSTEMS

Example:

atom in laser field



$$\hat{H}(\mathbf{t}) = \hat{T}_e + \hat{W}_{ee} + \sum_{j=1}^N -\frac{Ze^2}{r_j} + \vec{E} \cdot \vec{r}_j \cdot \cos \omega t$$

Weak laser ($v_{\text{laser}}(\mathbf{t}) \ll v_{\text{en}}$):

Calculate 1. Linear density response $\rho_1(\vec{r}, \omega)$

2. Dynamical polarizability

$$\alpha(\omega) = -\frac{e}{E} \int z \rho_1(\vec{r}, \omega) d^3 r$$

3. Photo-absorption cross section

$$\sigma(\omega) = -\frac{4\pi\omega}{c} \text{Im } \alpha$$

Strong laser ($v_{\text{laser}}(\mathbf{t}) > v_{\text{en}}$):

Aim: “Replace” full TDSE by TDKS scheme

Time-dependent density-functional formalism

E. Runge, E.K.U.G., Phys. Rev. Lett. 52, 997 (1984)

HK theorem: $v(r, t) \xleftrightarrow{1-1} \rho(r, t)$

The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables

KS theorem:

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(r, t) = \sum_{j=1}^N \left| \varphi_j(r, t) \right|^2$$

of an auxiliary non-interacting (KS) system

$$i\hbar \frac{\partial}{\partial t} \varphi_j(r, t) = \left[-\frac{\hbar^2 \nabla^2}{2m} + v_{\text{KS}}[\rho](r, t) \right] \varphi_j(r, t)$$

with the local potential

$$v_{\text{KS}}[\rho(r', t')](r, t) = v(r, t) + \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[\rho(\mathbf{r}', t')](\mathbf{r}, t)$$

Simplest possible approximation for $v_{xc}[\rho](\vec{r}, t)$

Adiabatic Local Density Approximation (ALDA)

$$v_{xc}^{ALDA}(\vec{r}, t) := v_{xc,stat}^{hom}(n) \Big|_{n=\rho(\vec{r}, t)}$$

$v_{xc,stat}^{hom}$ = **xc potential of static homogeneous e-gas**

Approximation with correct asymptotic $-1/r$ behavior: time-dependent optimized effective potential

C. A. Ullrich, U. Gossmann, E.K.U.G., PRL 74, 872 (1995)

Time-dependent DFT in the linear response regime and excited states

For times $t \leq t_0$:

System in ground state of $v_0(\mathbf{r})$
Density is the ground-state density $\rho_0(\mathbf{r})$

For times $t > t_0$:

Total external potential: $v(\mathbf{r}, t) = v_0(\mathbf{r}) + v_1(\mathbf{r}, t)$
(with $v_1(\mathbf{r}, t_0) = 0$)
density: $\rho(\mathbf{r}, t) = \rho_0(\mathbf{r}) + \delta\rho(\mathbf{r}, t)$

$$\delta\rho(\mathbf{r}, t) = \rho_1(\mathbf{r}, t) + \rho_2(\mathbf{r}, t) + \rho_3(\mathbf{r}, t) + \dots$$

↑
linear

↑
second order . . . density response to
the perturbation v_1

Standard Response Equation

$$v_1(\mathbf{r}, t) = \int dt' \int d^3r' \underbrace{\chi(\mathbf{r}, t, \mathbf{r}', t')}_{\text{full response function of the interacting (inhomogeneous) system}} v_1(\mathbf{r}', t')$$

full response function of the interacting (inhomogeneous) system

→ very hard to calculate

KS - Alternative

$$v_1(\mathbf{r}, t) = \int dt' \int d^3r' \underbrace{\chi_s(\mathbf{r}, t, \mathbf{r}', t')}_{\text{response function of the noninteracting (KS) system}} v_s^{(1)}(\mathbf{r}', t')$$

response function of the noninteracting (KS) system

→ relatively easy to calculate

self-consistent

$$\begin{aligned} v_s^{(1)}(\mathbf{r}, t) &= v_1(\mathbf{r}, t) + v_H^{(1)}(\mathbf{r}, t) + v_{xc}^{(1)}(\mathbf{r}, t) \\ &= v_1(\mathbf{r}, t) + \int d^3r' w(\mathbf{r}, \mathbf{r}') v_1(\mathbf{r}', t) + \int dt' \int d^3r' f_{xc}(\mathbf{r}, t, \mathbf{r}', t') v_1(\mathbf{r}', t') \end{aligned}$$

$f_{xc}(\mathbf{r}, t, \mathbf{r}', t')$ is the 1st-order term in a functional

Taylor expansion of $v_{xc}[\rho](\mathbf{r}, t)$ around $\rho_0(\mathbf{r})$:

$$v_{xc}[\rho](\mathbf{r}, t) = v_{xc}[\rho_0](\mathbf{r}, t) + \int dt' \int d^3r' \left. \frac{\delta v_{xc}(\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \right|_{\rho_0} (\rho(\mathbf{r}', t') - \rho_0(\mathbf{r}'))$$

Note: This is an exact representation of the linear density response

Standard linear response formalism

$H(t_0)$ = full static Hamiltonian at t_0

$H(t_0)|m\rangle = E_m |m\rangle$ ← exact many-body eigenfunctions and energies of system

full response function

$$\chi(r, r'; \omega) = \lim_{\eta \rightarrow 0^+} \sum_m \frac{\langle 0 | \hat{\rho}(r) | m \rangle \langle m | \hat{\rho}(r') | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{\rho}(r') | m \rangle \langle m | \hat{\rho}(r) | 0 \rangle}{\omega + (E_m - E_0) + i\eta}$$

⇒ The exact linear density response

$$\rho_1(\omega) = \hat{\chi}(\omega) v_1(\omega)$$

has poles at the exact excitation energies

$$\Omega = E_m - E_0$$

goal: Use the TDDFT representation of $\rho_1(\omega)$ to calculate the excitation energies:

$$\Omega = E_m + E_0$$

Excitation energies from TDDFT

exact representation of linear density response:

$$\chi_1(\omega) = \hat{\chi}_{\text{KS}}(\omega) \left(v_1(\omega) + \hat{W} \chi_1(\omega) + \hat{f}_{\text{xc}}(\omega) \chi_1(\omega) \right)$$

“ $\hat{}$ ” denotes integral operators

i.e. $\hat{f}_{\text{xc}} \chi_1 = \int f_{\text{xc}}(\vec{r}, \vec{r}') \chi_1(\vec{r}') d^3 r'$

where $\hat{\chi}_{\text{KS}}(\vec{r}, \vec{r}'; \omega) = \sum_{j,k} \frac{M_{jk}(\vec{r}, \vec{r}')}{-\left(\epsilon_j - \epsilon_k\right) + i}$

with

$$M_{jk}(\vec{r}, \vec{r}') = \left(f_k - f_j \right) \psi_j(\vec{r}) \psi_j^*(\vec{r}') - \psi_k(\vec{r}') \psi_k^*(\vec{r})$$

$$f_m = \begin{cases} 1 & \text{if } m \text{ is occupied in KS ground state} \\ 0 & \text{if } m \text{ is unoccupied in KS ground state} \end{cases}$$

$\epsilon_j - \epsilon_k$ KS excitation energy

$$\left(\hat{1} - \hat{K}_S(\epsilon) \left[\hat{W}_{\text{Clb}} + \hat{f}_{\text{xc}}(\epsilon) \right] \right) \psi_1(\epsilon) = \hat{K}_S(\epsilon) \psi_1(\epsilon)$$

$\psi_1(\epsilon)$ for (exact excitation energy) but right-hand side remains finite for

hence

$$\left(\hat{1} - \hat{K}_S(\epsilon) \left[\hat{W}_{\text{Clb}} + \hat{f}_{\text{xc}}(\epsilon) \right] \right) \psi_1(\epsilon) = \psi_1(\epsilon) \psi_1(\epsilon)$$

$$\psi_1(\epsilon) = 0 \text{ for}$$

This condition rigorously determines the exact excitation energies, i.e.,

$$\left(\hat{1} - \hat{K}_S(\epsilon) \left[\hat{W}_{\text{Clb}} + \hat{f}_{\text{xc}}(\epsilon) \right] \right) \psi_1(\epsilon) = 0$$

This equation is rigorously equivalent to:

(See T. Grabo, M. Petersilka, E. K. U. G., J. Mol. Struct. (Theochem) 501, 353 (2000))

$$\left(A_{qq'} + \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}') \right) q' = q$$

where

$$A_{qq'} = \int d^3r \int d^3r' q(\mathbf{r})$$

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}') q'(\mathbf{r}')$$

$q = (j, k)$ **double index**

$$q(\mathbf{r}) = f_k^*(\mathbf{r}) - f_j(\mathbf{r})$$

$$q = f_k - f_j$$

$$q = k - j$$

Single-pole approximation

Expand all quantities about one KS pole

$$\left(\begin{array}{c} j_0 \\ - \\ k_0 \end{array} \right)$$

$$\hat{\chi}_{\text{KS}} \left(\begin{array}{c} j_0 \\ - \\ k_0 \end{array} \right) = \frac{M_{j_0 k_0}}{-\left(\begin{array}{c} j_0 \\ - \\ k_0 \end{array} \right) + i} + \text{higher order terms}$$

$$= \left(\begin{array}{c} j_0 \\ - \\ k_0 \end{array} \right) + K$$

$$K = \int d^3 r \int d^3 r' \chi_{j_0}(\mathbf{r}) \chi_{j_0}^*(\mathbf{r}') \chi_{k_0}(\mathbf{r}') \chi_{k_0}^*(\mathbf{r})$$

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}')$$

Atom	Experimental Excitation Energies ${}^1S \rightarrow {}^1P$ (in Ry)	KS energy differences $\Delta\epsilon_{KS}$ (Ry)	$\Delta\epsilon_{KS} + K$
Be	0.388	0.259	0.391
Mg	0.319	0.234	0.327
Ca	0.216	0.157	0.234
Zn	0.426	0.315	0.423
Sr	0.198	0.141	0.210
Cd	0.398	0.269	0.391

from: M. Petersilka, U. J. Gossmann, E.K.U.G., PRL 76, 1212 (1996)

$$\Delta E = \underbrace{\Delta\epsilon_{KS}}_{\epsilon_j - \epsilon_k} + K$$

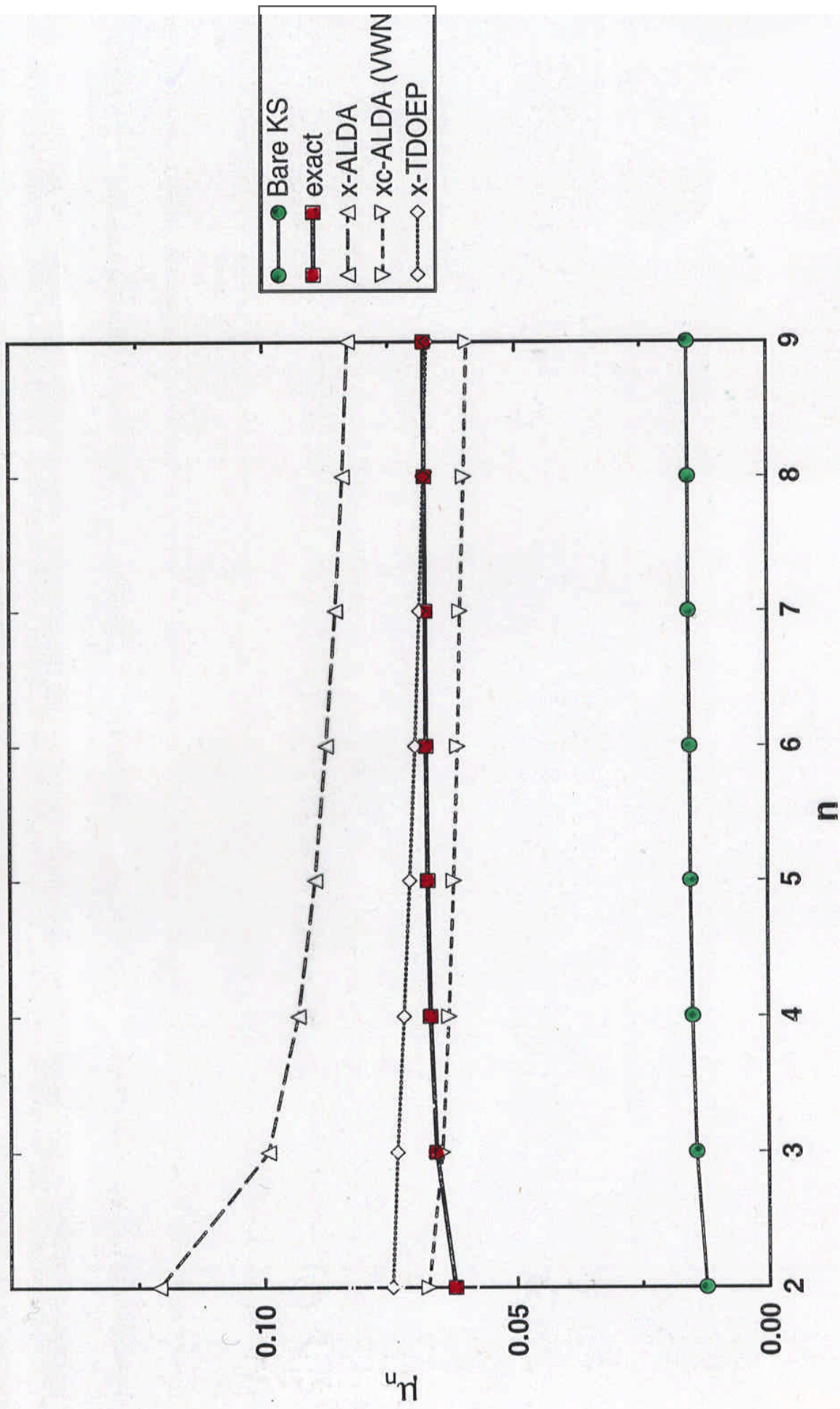
$$K = \int d^3r \int d^3r' \varphi_j(r) \varphi_j^*(r') \varphi_k(r) \varphi_k^*(r') \left(\frac{1}{|r-r'|} + f_{xc}(r, r') \right)$$

Excitation energies of CO molecule

	State	Ω_{expt}	KS-transition	$\Delta\epsilon_{\text{KS}}$	$\Delta\epsilon_{\text{KS}} + \text{K}$
A	${}^1\Pi$	0.3127	$5\Sigma \rightarrow 2\Pi$	0.2523	0.3267
a	${}^3\Pi$	0.2323			0.2238
I	${}^1\Sigma^-$	0.3631	$1\Pi \rightarrow 2\Pi$	0.3626	0.3626
D	${}^1\Delta$	0.3759			0.3812
a'	${}^3\Sigma^+$	0.3127			0.3181
e	${}^3\Sigma^-$	0.3631			0.3626
d	${}^3\Delta$	0.3440			0.3404

approximations made: $v_{\text{xc}}^{\text{LDA}}$ and $f_{\text{xc}}^{\text{ALDA}}$

Quantumdefects in Helium 3P Series



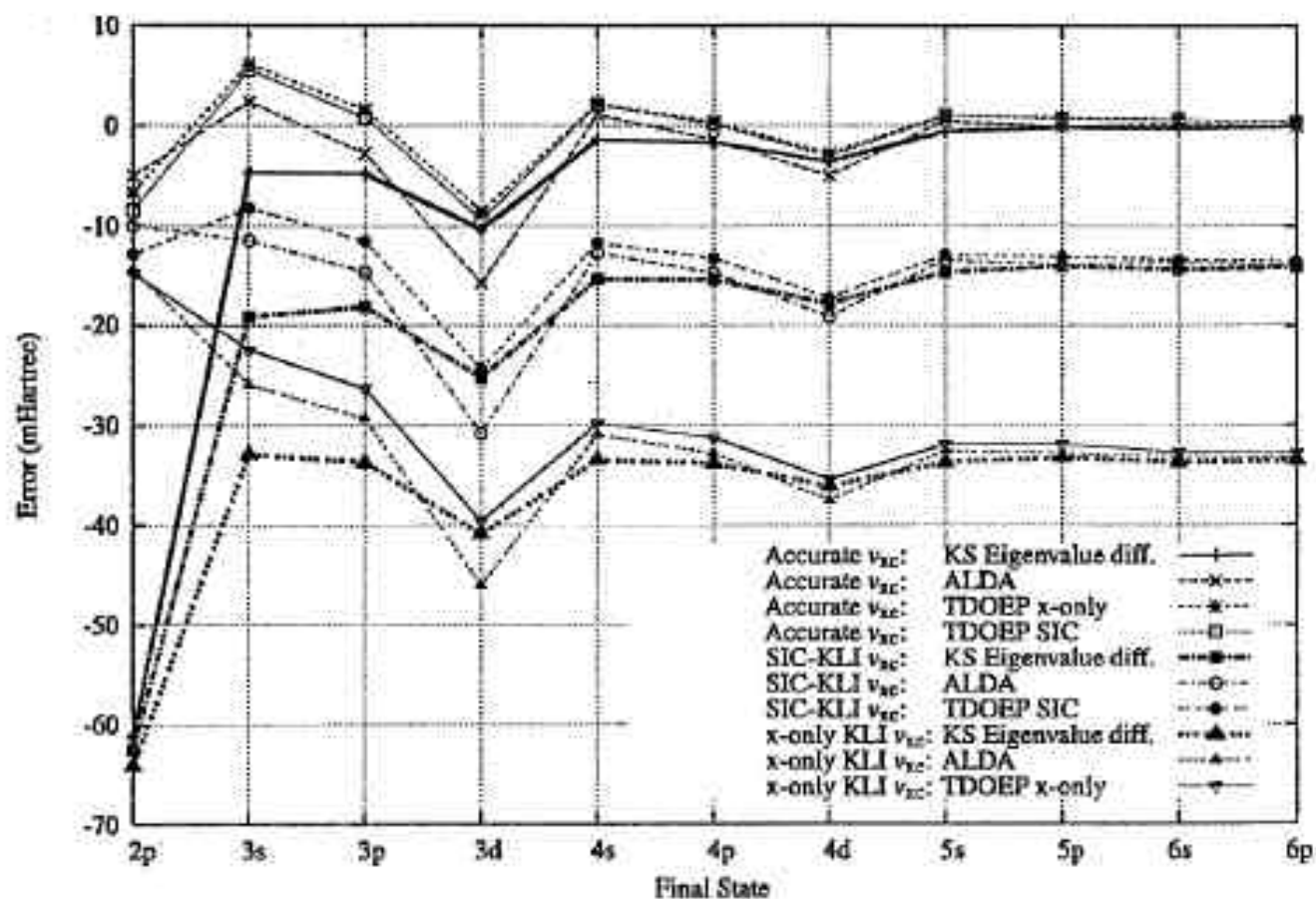
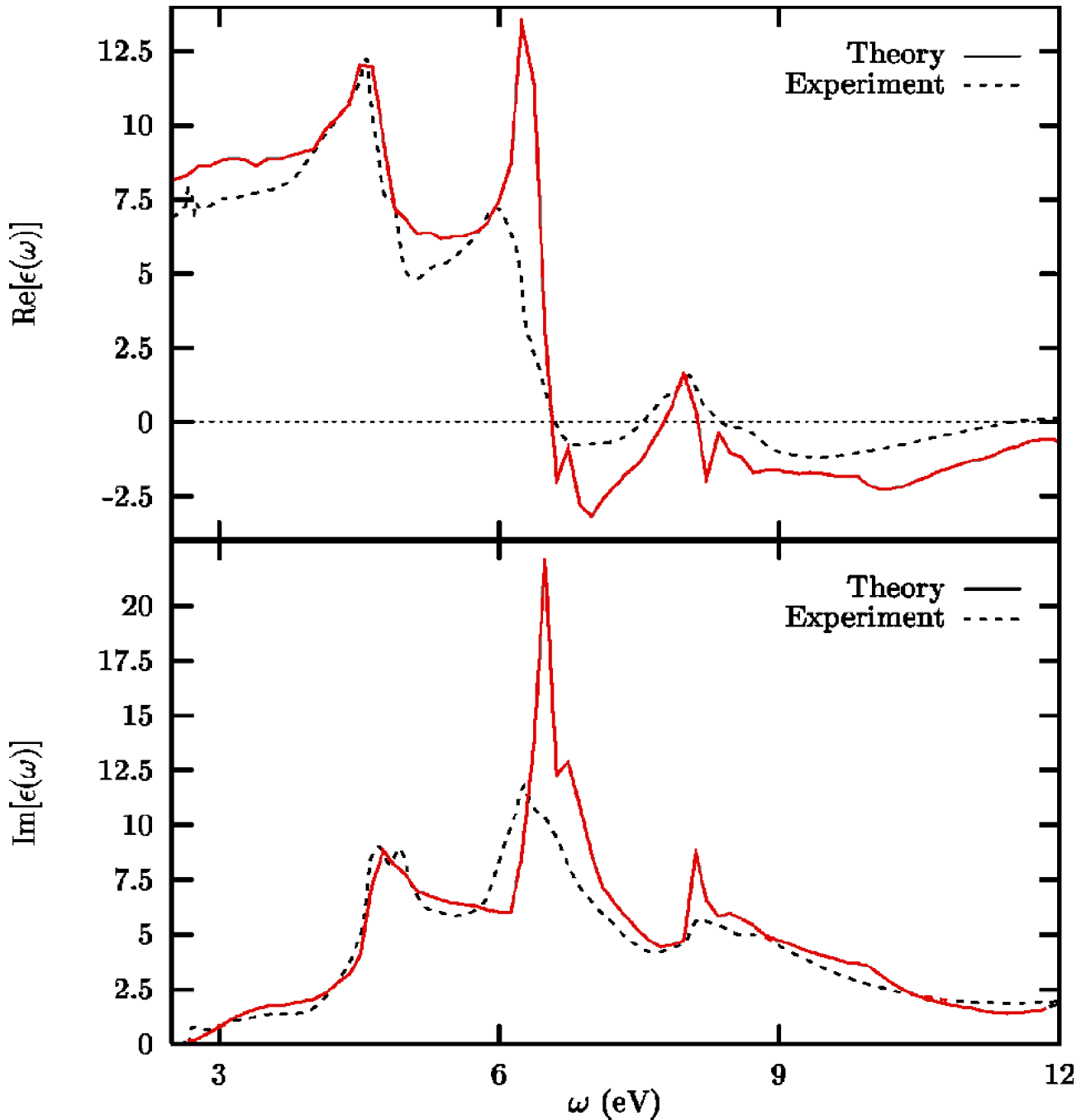


Figure 3.3: Errors of singlet excitation energies from the ground state of Be, calculated from the accurate, the OEP-SIC and x-only KLI exchange correlation potential and with different approximations for the exchange-correlation kernel (see text). The errors are given in mHartrees. To guide the eye, the errors of the discrete excitation energies were connected with lines.

Dielectric Function Zinc selenide (ZnSe)

Kootstra, de Boeij, Snijders, Phys. Rev. B 62, 7071 (2000)



Experimental data taken from: J.L. Freilouf, Phys. Rev. B 7, 3810 (1973)

Failures of ALDA in the linear response regime

- **H₂ dissociation is incorrect:**

$$E\left(1^+_{\text{u}}\right) - E\left(1^+_{\text{g}}\right) \approx 0 \quad \text{(in ALDA)}$$

(see: Gritsenko, van Gisbergen, Görling, Baerends, J. Chem. Phys. 113, 8478 (2000))

- **response of long chains strongly overestimated**

(see: Champagne et al., J. Chem. Phys. 109, 10489 (1998) and 110, 11664 (1999))

- **in periodic solids, $f_{\text{xc}}^{\text{ALDA}}(q, \omega) = c(\omega)$**

whereas, for insulators, $f_{\text{xc}}^{\text{exact}}(q, \omega) \sim 1/q^2$

divergent.

DEFICIENCIES OF LDA/GGA

- Not free from spurious self-interactions
KS potential decays more rapidly than r^{-1}

Consequences: – no Rydberg series

- negative atomic ions not bound
- ionization potentials (if calculated from highest occupied orbital energy) too small

- Dispersion forces cannot be described

$$W_{\text{int}}(R) \longrightarrow e^{-R} \text{ (rather than } R^{-6}\text{)}$$

- band gaps too small:

$$E_{\text{gap}}^{\text{LDA}} \approx 0.5 E_{\text{gap}}^{\text{exp}}$$

- Cohesive energies of bulk metals not satisfactory

in LDA overestimated

in GGA underestimated

- Wrong ground state for strongly correlated solids, e.g. FeO , La_2CuO_4 predicted as metals

3 generations of approximations for E_{xc}

1. Local Density Approximation:

$$E_{xc}^{LDA} = \int^3 r e_{xc}^{hom}(\rho(r))$$

2. Generalized Gradient Approximation:

$$E_{xc}^{GGA} = \int^3 r g_{xc}(\rho, \nabla \rho, \dots)$$

3. Orbital functionals:

$$E_{xc}^{OPM} = E_{xc}[\phi_1 \dots \phi_N]$$

(Optimized Effective Potential Method: OPM, OEP)

Apply HK theorem to non-interacting particles

given $v_s = v_s[\rho]$ $\left(-\frac{\hbar^2}{2m} \nabla^2 + v_s[\rho](\mathbf{r})\right) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$
 $\rho = \sum_i |\varphi_i|^2$, $\epsilon_i = \epsilon_i[\rho]$

consequence:

Any orbital functional, $E_{xc}[\varphi_1, \varphi_2, \dots]$, is an (implicit) density functional provided that the orbitals come from a local (i.e., multiplicative) potential.

“optimized effective potential” KS xc potential

$$v_{xc}^{\text{OPM}}(\mathbf{r}) = \frac{\delta E_{xc}[\varphi_1, \dots, \varphi_N]}{\delta \rho(\mathbf{r})}$$

$$v_{xc}^{\text{OPM}}(\mathbf{r}) = \sum_j \int d^3 r' \int d^3 r'' \frac{E_{xc}(\mathbf{r}', \mathbf{r}'')}{\varphi_j(\mathbf{r}') \varphi_j(\mathbf{r}'')} \underbrace{\frac{v_s(\mathbf{r}'')}{\rho(\mathbf{r})}}_{\chi_{\text{KS}}^{-1}(\mathbf{r}'', \mathbf{r})} + \text{c.c.}$$

act with χ_{KS} on equation:

$$\int \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}') v_{xc}^{\text{OPM}}(\mathbf{r}') d^3 r' = \sum_j \int d^3 r' \frac{E_{xc}(\mathbf{r}', \mathbf{r}')}{\varphi_j(\mathbf{r}') \varphi_j(\mathbf{r}')} + \text{c.c.}$$

OPM integral equation

known functional of $\{\varphi_j\}$

OPM integral equation

$$\sum_{i=1}^N \int d^3r' (V_{xc, OPM}(r') - u_{xc,i}(r')) K_i(r, r') \psi_i(r) \psi_i^*(r') + c.c. = 0$$

$$\text{where } K_i(r, r') = \sum_{k=1}^k \frac{\psi_k^*(r) \psi_k(r')}{\epsilon_{ks} - \epsilon_{is}}$$

$$\text{and } u_{xc,i}(r) := \frac{1}{\psi_i^*(r)} \frac{E_{xc}[\psi_i, \dots]}{\psi_i(r)}$$

to be solved simultaneously with KS equation:

$$\left(-\frac{\nabla^2}{2} + v_o(r) + \int \frac{v(r')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc, OPM}(r)\right) \psi_j(r) = \epsilon_j \psi_j(r)$$

Total absolute ground-state energies for first-row atoms from various self-consistent calculations. All numbers in hartree. (OPM values from T. Grabo, E.K.U.G., Chem. Phys. Lett. 240, 141 (1995))

	OPM	BLYP	PW91	QCI	EXACT
He	2.9033	2.9071	2.9000	2.9049	2.9037
Li	7.4829	7.4827	7.4742	7.4743	7.4781
Be	14.6651	14.6615	14.6479	14.6657	14.6674
B	24.6564	24.6458	24.6299	24.6515	24.6539
C	37.8490	37.8430	37.8265	37.8421	37.8450
N	54.5905	54.5932	54.5787	54.5854	54.5893
O	75.0717	75.0786	75.0543	75.0613	75.067
F	99.7302	99.7581	99.7316	99.7268	99.734
Ne	128.9202	128.9730	128.9466	128.9277	128.939
-	0.0047	0.0108	0.0114	0.0045	

Comparison: $\bar{\quad}(\text{LDA}) = 0.383$
 $\bar{\quad}(\text{HF}) = 0.177$

- $\bar{\quad}$: Mean absolute deviation from the exact nonrelativistic values.
- QCI: Complete basis set quadratic configuration-interaction/atomic pair natural orbital model: J.A. Montgomery, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 101, 5900 (1994).
- EXACT: E.R. Davison, S.A. Hagstrom, S.J. Chakravorty, V.M. Umar, C. Froese Fischer, Phys. Rev. A 44, 7071 (1991).

Approximation employed for E_{xc} :

$E_x[\varphi_1 \dots \varphi_N] = \text{exact Fock term}$

$E_c[\varphi_1 \dots \varphi_N] = \text{Colle-Salvetti functional}$

Total absolute ground-state energies for second-row atoms from various self-consistent calculations. All numbers in hartree. (OPM values from T. Grabo, E.K.U.G., Chem. Phys. Lett. 240, 141 (1995))

	OPM	BLYP	PW91	EXPT
Na	162.256	162.293	162.265	162.257
Mg	200.062	200.093	200.060	200.059
Al	242.362	242.380	242.350	242.356
Si	289.375	289.388	289.363	289.374
P	341.272	341.278	341.261	341.272
S	398.128	398.128	398.107	398.139
Cl	460.164	460.165	460.147	460.196
Ar	527.553	527.551	527.539	527.604
–	0.013	0.026	0.023	

- –: Mean absolute deviation from Lamb-shift corrected experimental values, taken from R.M. Dreizler and E.K.U.G., Density functional theory: an approach to the quantum many-body problem (Springer, Berlin, 1990).

Helium Isoelectronic Series

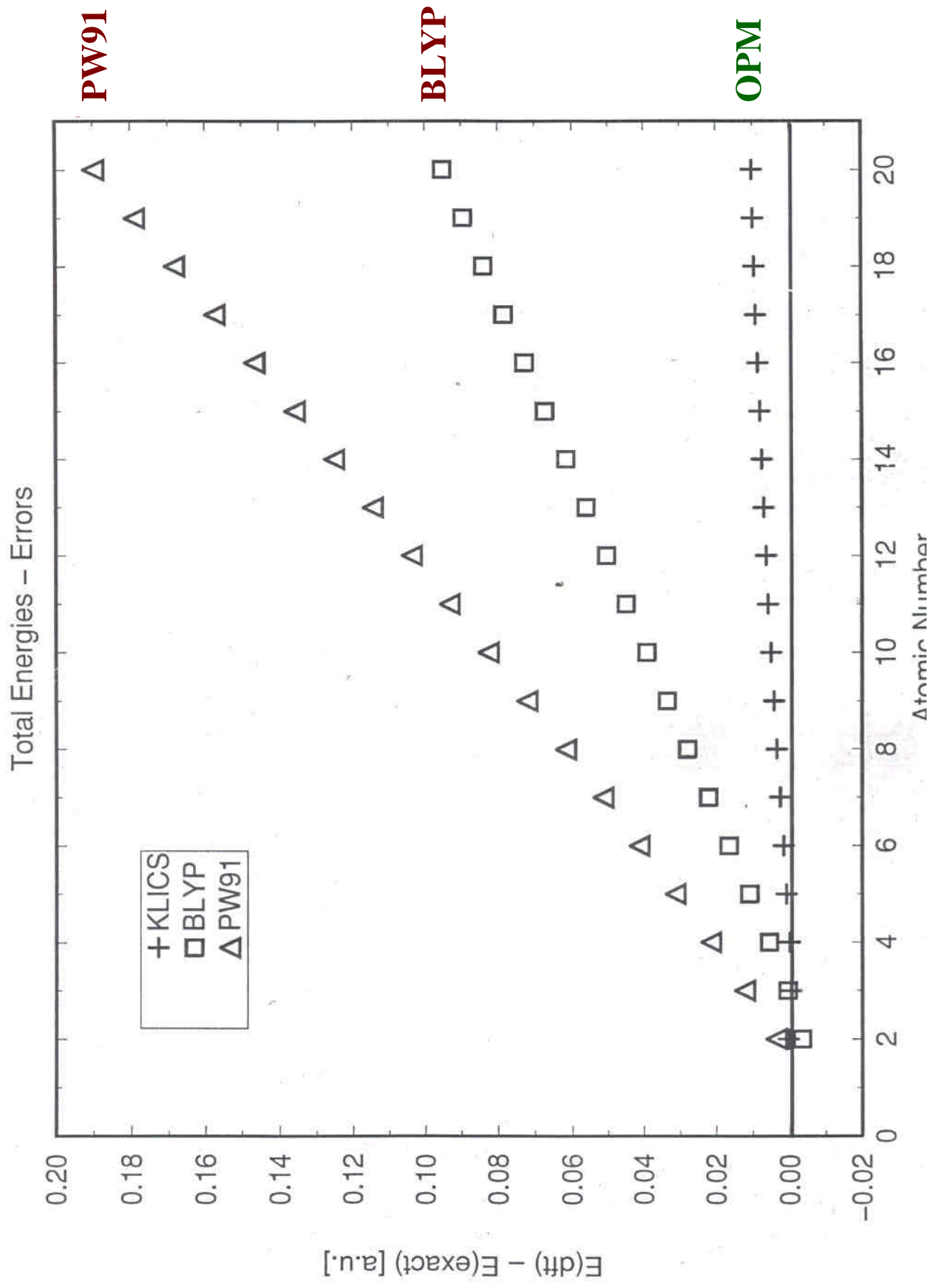


Table 3

Ionization potentials from the highest occupied orbital energy of neutral atoms. $\bar{\Delta}$ denotes the mean absolute deviation from the experimental values, taken from [56]. All values in atomic units. Taken from [31] and modified.

	OPM KLICS	xcLDA	GGA's BLYP	PW91	experiment
He	0.945	0.570	0.585	0.583	0.903
Li	0.200	0.116	0.111	0.119	0.198
Be	0.329	0.206	0.201	0.207	0.343
B	0.328	0.151	0.143	0.149	0.305
C	0.448	0.228	0.218	0.226	0.414
N	0.579	0.309	0.297	0.308	0.534
O	0.559	0.272	0.266	0.267	0.500
F	0.714	0.384	0.376	0.379	0.640
Ne	0.884	0.498	0.491	0.494	0.792
Na	0.189	0.113	0.106	0.113	0.189
Mg	0.273	0.175	0.168	0.174	0.281
Al	0.222	0.111	0.102	0.112	0.220
Si	0.306	0.170	0.160	0.171	0.300
P	0.399	0.231	0.219	0.233	0.385
S	0.404	0.228	0.219	0.222	0.381
Cl	0.506	0.305	0.295	0.301	0.477
Ar	0.619	0.382	0.373	0.380	0.579
$\bar{\Delta}$	0.030	0.176	0.183	0.177	

functional: $E_x^{\text{exact}} + E_c^{\text{LDA}}$

TABLE II. Comparison of theoretical LDA and EXX Kohn-Sham eigenvalue gaps (in eV) and total valence band widths (VBW, in eV) with experimental data, taken from Ref. 73 except where otherwise noted. The gaps have been calculated at the experimental lattice constants and are given relative to the top of the valence band. Si* refers to a calculation with a local pseudopotential. The experimental data have been corrected for spin-orbit splitting effects since the latter are not included in the calculations.

	LDA				EXX				Expt.			
	L	Γ	X	VBW	L	Γ	X	VBW	L	Γ	X	VBW
Si*	1.54	2.79	0.52	12.77	2.36	3.46	1.43	12.34	2.4	3.34	1.25 ^c	12.5
Si	1.43	2.56	0.64	11.95	2.35	3.26	1.50	11.58				
Ge	0.13	-0.09	0.75	12.86	1.01	1.28	1.34	12.48	0.84	1.00	1.3	12.6
C	8.43	5.56	4.78	21.29	9.18	6.28	5.43	21.52		7.3 ^b		24.2 ^c
GaAs	0.89	0.32	1.41	12.78	1.93	1.82	2.15	12.33	1.85	1.63	2.18	13.1
AlAs	2.03	1.84	1.37	11.89	2.99	3.20	2.26	11.53	2.54	3.11	2.24	
SiC	5.36	6.33	1.36	15.32	6.30	7.17	2.52	15.21		7.59 ^c	2.39	
GaN	4.58	1.90	3.38	15.75	6.21	3.49	4.95	15.64		3.30 ^d		
AlN	7.16	4.20	3.24	14.74	8.58	5.66	5.03	14.86				

^aReference 88.

^bReference 89.

^cReference 90.

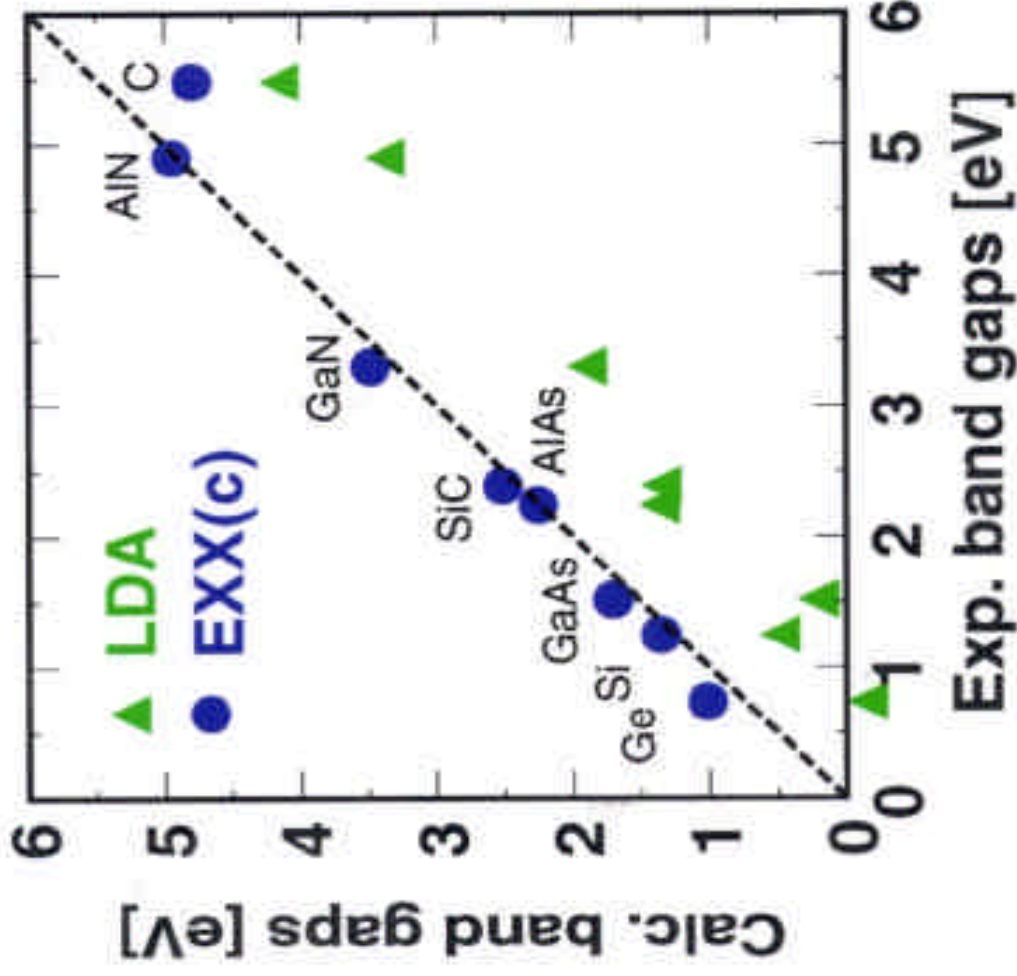
^dReference 91.

M. Städele, M. Moukara, J. A. Majewski, and P. Vogl and A. Görling, PRB 59, 10031 (1999)

TABLE IX. Comparison of energy gaps between occupied and empty states with experiment. All energies in eV.

	LDA	GW-LDA	EXX	GW-EXX	Experiment
Si					
E_g	0.51	1.19	1.43	1.54	1.17 ^a
E'_0	2.55	3.23	3.28	3.57	3.35 ^b
E_1	2.69	3.38	3.35	3.72	3.46 ^b
E'_1	4.52	5.26	5.08	5.57	5.38 ^b
E_2	3.48	4.18	4.12	4.51	4.32 ^b
Ge					
$E_g(L_c - \Gamma_v)$	0.06	0.62	0.86	0.94	0.74 ^a
E_0	-0.07	0.57	0.81	0.94	0.90 ^c
\bar{E}'_0	2.59	3.17	3.16	3.40	3.16 ^c
E_1	1.44	2.03	2.14	2.32	2.22 ^c
E_2	3.75	4.31	4.37	4.56	4.45 ^c
GaAs					
E_0	0.49	1.22	1.49	1.65	1.52 ^d
E'_0	3.55	4.24	4.16	4.51	4.51 ^d
E_1	2.02	2.73	2.80	3.09	3.04 ^d
E_2	3.98	4.65	4.72	4.99	5.13 ^d
BeSe					
E_0	4.04	5.46	5.25	5.92	5.55 ^e
\bar{E}'_0	5.01	6.48	5.78	6.75	7.29 ^c
E_1	5.18	6.57	6.00	6.95	6.15 ^c
E'_1	6.81	8.31	7.48	8.64	8.47 ^c
E_2	5.02	6.43	5.86	6.82	6.56 ^c
BeTe					
$E_g(X_c - \Gamma_v)$	1.60	2.59	2.47	2.88	2.7 ^f , 2.8 ^g
E_0	3.28	4.33	3.91	4.58	4.20 ^h
E_1	3.97	4.97	4.61	5.28	4.69 ^h
E_2	4.33	5.37	4.99	5.68	5.04 ^h
MgSe					
E_0	2.47	4.08	3.72	4.71	4.23 ⁱ
MgTe					
E_0	2.29	3.66	3.33	4.20	3.67 ⁱ

Fundamental Energy gaps



- **EXX** gives excellent band gaps: larger than LDA by ~ 1 eV
- Small influence of correlation
- **EXX** pseudopotential important for Ge: minimum of conduction band in L

from: Städele et al., Phys. Rev. B 59, 10031 (1999)

Fundamental band gap in semiconductors and insulators

Hartree-Fock

$$\begin{aligned}\text{gap } \Delta^{\text{HF}} &= E^{\text{HF}}(N+1) - 2 E^{\text{HF}}(N) + E^{\text{HF}}(N-1) \\ &= \epsilon_{N+1}^{\text{HF}}(N) - \epsilon_N^{\text{HF}}(N)\end{aligned}$$

DFT with exact exchange (OPM)

$$\begin{aligned}\text{gap } \Delta_{x\text{-only}}^{\text{OPM}} &= E^{\text{OPM}}(N+1) - 2 E^{\text{OPM}}(N) + E^{\text{OPM}}(N-1) \\ &= \epsilon_{N+1}^{\text{KS}}(N) - \epsilon_N^{\text{KS}}(N) + D_{x\text{-only}}\end{aligned}$$

↑
discontinuity of v_x

$$E^{\text{HF}} \approx E^{\text{OPM}} \quad \Rightarrow \quad \Delta^{\text{HF}} \approx \Delta_{x\text{-only}}^{\text{OPM}}$$

**Orbital functionals for
the static xc energy
derived from TDDFT**

ADIABATIC CONNECTION FORMULA

$$H(\mathbf{1}) = T + \sum_{i=1}^N v_{\mathbf{1}}(\mathbf{r}_i) + \mathbf{1} \frac{e^2}{2} \sum_{i,k=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_k|} \quad \mathbf{0} \leq \mathbf{1} \leq \mathbf{1}$$

$$H(\mathbf{1}=\mathbf{1}) = T + \sum_{i=1}^N v_{\text{nuc}}(\mathbf{r}_i) + \frac{e^2}{2} \sum_{i,k=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_k|}$$

= Hamiltonian of fully interacting system

Choose $v(\mathbf{r})$ such that for each $\mathbf{1}$ the ground-state density satisfies $n(\mathbf{r}) = n_{\mathbf{1}}(\mathbf{r})$

Hence

$$v_{\mathbf{1}=0}(\mathbf{r}) = v_{\text{KS}}(\mathbf{r})$$

$$v_{\mathbf{1}=1}(\mathbf{r}) = v_{\text{nuc}}(\mathbf{r})$$

Determine the response function $\chi^{(1)}(\mathbf{r}, \mathbf{r}'; \omega)$ corresponding to $H(\mathbf{1})$, Then

$$E_{\text{xc}} = - \int_0^1 d\lambda \int_0^{\infty} \frac{d\omega}{2} \int d^3 r \int d^3 r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \left\{ \chi^{(1)}(\mathbf{r}, \mathbf{r}'; i\omega) + n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right\}$$

Second ingredient : TDDFT

$$\begin{aligned} \chi_1 &= \chi_s \mathbf{V}_{s,1} = \chi_s \left(\mathbf{V}_1 + [\mathbf{W}_{\text{clb}} + \mathbf{f}_{\text{xc}}] \chi_1 \right) \\ \chi_1 &= \mathbf{V}_1 \end{aligned}$$

$$\mathbf{V}_1 = \chi_s \left(\mathbf{V}_1 + [\mathbf{W}_{\text{clb}} + \mathbf{f}_{\text{xc}}] \chi_s \right)$$

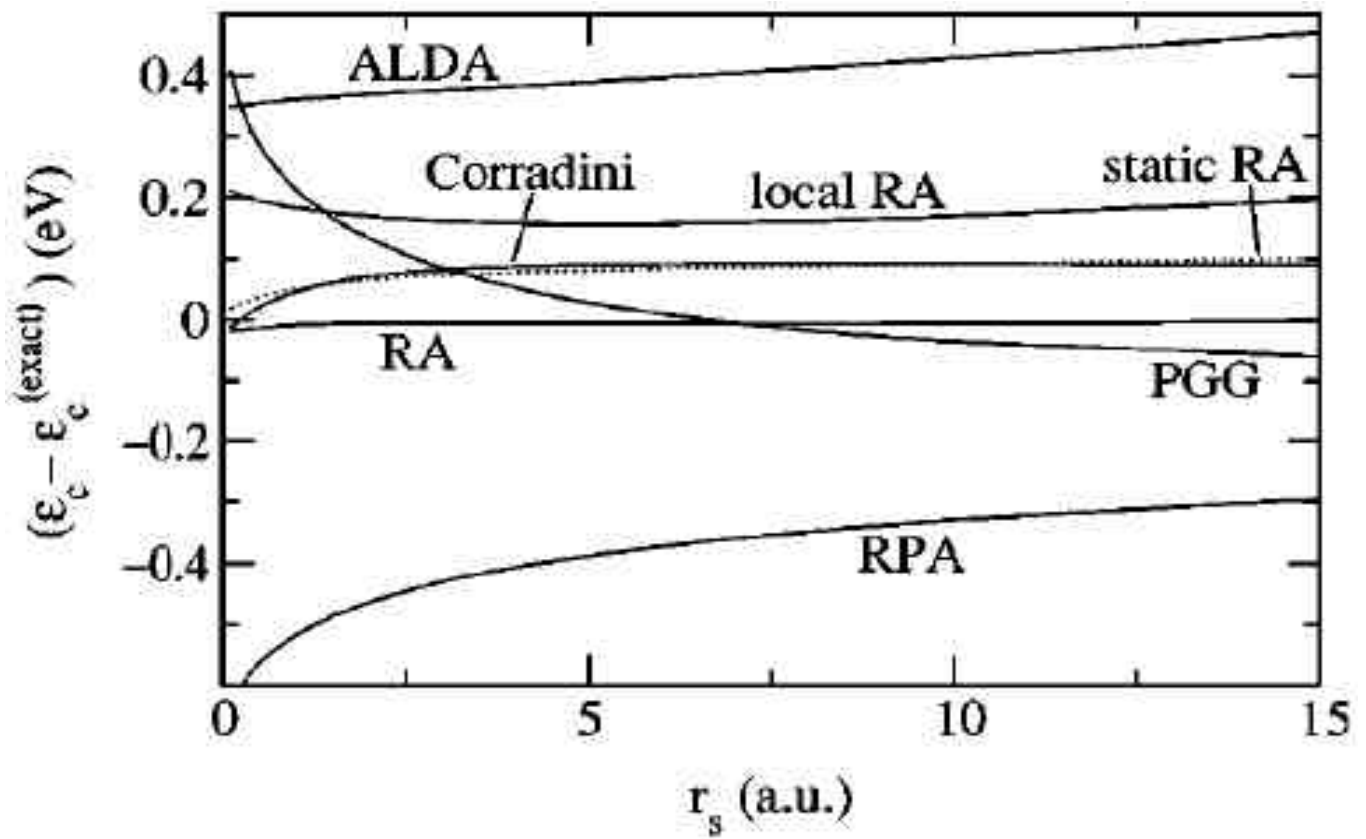
$$\Rightarrow \boxed{\chi_1 = \chi_s + \chi_s [\mathbf{W}_{\text{clb}} + \mathbf{f}_{\text{xc}}] \chi_s}$$

truncate after first iteration:

$$\chi^{(\lambda)} \approx \chi_s + \chi_s [\lambda \mathbf{W}_{\text{clb}} + \mathbf{f}_{\text{xc}}^{(\lambda)}] \chi_s$$

**plug this approximation into adiabatic connection formula,
integrations over λ and ω can be done analytically**

\Rightarrow Orbital functional for E_c



r_s -dependent deviation of approximate correlation energies from the “exact” correlation energy per electron of the uni-form electron.

M. Lein, E. K. U. G., J. Perdew, Phys. Rev. B 61, 13431 (2000).

truncate after first iteration:

$$\chi^{(\lambda)} \approx \chi_s + \chi_s [\lambda \mathbf{W}_{\text{clb}} + \mathbf{f}_{\text{xc}}^{(\lambda)}] \chi_s$$

plug this approximation into adiabatic connection formula, integrations over λ and ω can be done analytically

\Rightarrow Orbital functional for E_c

Resulting Atomic Correlation energies (in a.u.)

atom	LDA	new fctl	exact
He	-0.111	-0.048	-0.042
Be	-0.224	-0.13	-0.096
Ne	-0.739	-0.41	-0.394
Ar	-1.423	-0.67	-0.72

Resulting v.d.W. coefficients C_6

system	Calculated C_6	experiment
He-He	1.639	1.458
He-Ne	3.424	3.029
Ne-Ne	7.284	6.383
Li-Li	1313	1390
Li-Na	1453	1450
Na-Na	1614	1550
H-He	2.995	2.82
H-Ne	5.976	5.71
H-Li	64.96	66.4
H-Na	75.4	71.8

Lein, Dobson, EKUG, J. Comp. Chem. ('99)

Review articles on time-dependent DFT/excitation energies, and OPM

Density-functional theory of time-dependent phenomena. E. K. U. Gross, J. F. Dobson. M. Petersilka, in: *Topics in Current Chemistry*, vol. 181, edited by R. Nalewajski (Springer, 1996), p. 81-172

A guided tour of time-dependent DFT. K. Burke, E. K. U. Gross, in: *Springer Lectures Notes in Physics*, vol. 500 (1998), p. 116-146

Orbital functionals in density functional theory: the optimized effective potential method. T. Grabo, T. Kreibich, S. Kurth, E.K.U. Gross, in: *Strong Coulomb Correlations in Electronic Structure: Beyond the LDA*, edited by V.I. Anisimov Gordon & Breach (2000), p. 203-311.

DICHROISM IN THE FREQUENCY-DEPENDENT RESPONSE OF SUPERCONDUCTORS

E. K. U. GROSS
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OUTLINE

1. Relativistic theory of superconductivity
2. Dichroism in Superconductors

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Relativistic Effects in Superconductors

$$\hat{H}^{nonrel} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \left[\frac{\left(-i\vec{\nabla} + \frac{e}{c}\vec{A} \right)^2}{2m} + (v(\mathbf{r}) - \mu) \right] \hat{\psi}_{\sigma}(\mathbf{r})$$

$$- \int d^3r \int d^3r' \left(\Delta^*(\mathbf{r}, \mathbf{r}') \hat{\chi}(\mathbf{r}, \mathbf{r}') + \Delta(\mathbf{r}, \mathbf{r}') \hat{\chi}^{\dagger}(\mathbf{r}, \mathbf{r}') \right)$$

$$\hat{H}^{rel} = \int d^3r \hat{\Psi}(\mathbf{r}) \left[c\vec{\gamma} \cdot (-i\vec{\nabla}) + mc^2 + \gamma_{\mu} A^{\mu} \right] \hat{\Psi}(\mathbf{r})$$

+ ?

$\hat{\Psi}(\mathbf{r}) =$ Dirac spinor field operator

QUESTION: What is the correct relativistic generalization of the non-relativistic order parameter $\hat{\chi}(\mathbf{r}, \mathbf{r}')$?

non-relativistic order parameter

homogeneous case: $\vec{k} = \langle \hat{a}_{\vec{k}} \hat{a}_{-\vec{k}} \rangle$

spherical case: $l,m = \langle \hat{a}_{l,m} \hat{a}_{l,-m} \rangle$

general case: $= \langle \hat{a}_{\text{state}} \hat{a}_{\text{time-reversed state}} \rangle$

(Kramers pair)

require relativistic generalization of order parameter to be a Kramers pair

$$\hat{\alpha}_{\text{rel}}(\mathbf{r}, \mathbf{r}') = \hat{\alpha}^t(\mathbf{r}) T \hat{\alpha}(\mathbf{r}')$$

with time reversal operator

$$T = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$$

Resulting relativistic order parameter $\hat{\alpha}_{\text{rel}}$ is Lorentz scalar

$$\hat{H}_{\text{rel}} = \int d^3r \hat{\alpha}(\mathbf{r}) \left(c \left(-i \frac{\partial}{\partial t} \right) + mc^2 + A \right) \hat{\alpha}(\mathbf{r}) - \int d^3r \int d^3r' \left(\hat{\alpha}^*(\mathbf{r}, \mathbf{r}') \hat{\alpha}_{\text{rel}}(\mathbf{r}, \mathbf{r}') + \text{H.C.} \right)$$

DIRAC EQUATION FOR SUPERCONDUCTORS

$$\hat{\gamma}^0 \left[c \vec{\gamma} \cdot \vec{p} + mc^2 (1 - \hat{\gamma}^0) + q \gamma^\mu A_\mu \right] u_n(\mathbf{r}) + \int d^3 \mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \hat{\eta}_0 v_n(\mathbf{r}') = E_n u_n(\mathbf{r})$$

$$-\hat{\gamma}^0 \left[c \vec{\gamma} \cdot \vec{p} + mc^2 (1 - \hat{\gamma}^0) + q \gamma^\mu A_\mu \right]^* v_n(\mathbf{r}) - \int d^3 \mathbf{r}' \Delta^*(\mathbf{r}, \mathbf{r}') \hat{\eta}_0 u_n(\mathbf{r}') = E_n v_n(\mathbf{r})$$

Particle amplitudes u_n }
 Hole amplitudes v_n } are Dirac spinors

special case

uniform system: $v(\mathbf{r}) = \text{const}$ 0

$$G(\mathbf{r}, \mathbf{r}') = G(\mathbf{r} - \mathbf{r}') = \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \tilde{G}(\mathbf{k}) e^{i\mathbf{k}(\mathbf{r} - \mathbf{r}')}$$

no magnetic fields: $\vec{A}(\mathbf{r}) = 0$

spectrum

$$E_{\mathbf{k}} = \pm \sqrt{\left(\pm \sqrt{\hbar^2 \mathbf{k}^2 c^2 + m^2 c^4} - mc^2 - \mu \right)^2 + |\tilde{G}(\mathbf{k})|^2}$$

$E_{\mathbf{k}} \approx 0$ Dirac spectrum (for particles and holes)

$E_{\mathbf{k}} \approx \hbar \mathbf{k} \cdot \mathbf{v} < mc$ BCS spectrum

Non-relativistic limit of Dirac BdG equations

$$\underbrace{\begin{pmatrix} \left[\frac{(\vec{\sigma} \cdot \vec{\pi})^2}{2m} + (v(r) - \mu) \right] & \Delta(\mathbf{r})(i\sigma_y) \\ (-i\sigma_y)\Delta^*(\mathbf{r}) & -\left[\frac{(\vec{\sigma}^* \cdot \vec{\pi}^*)^2}{2m} + (v(r) - \mu) \right] \end{pmatrix}}_{H_0} \begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix} = E \begin{pmatrix} u(\mathbf{r}) \\ v(\mathbf{r}) \end{pmatrix}$$

$u(\mathbf{r})$ and $v(\mathbf{r})$ are PAULI spinors, and

weakly relativistic limit, up to order $(v/c)^2$

$$(H_0 + H_2) \begin{pmatrix} u \\ v \end{pmatrix} = E \begin{pmatrix} u \\ v \end{pmatrix}$$

$$H_2 = \begin{pmatrix} h_2 & d_2 \\ d_2^+ & -h_2^* \end{pmatrix}$$

$$h_2 = \frac{1}{4m^2c^2} \left(\frac{\hbar^2}{2} \nabla^2 v + \hbar \vec{\sigma} \cdot (\vec{\nabla} v) \times \vec{p} - \frac{p^4}{2m} \right)$$

$$d_2 = \frac{1}{4m^2c^2} \left(\frac{\hbar^2}{2} \nabla^2 \Delta + \hbar \vec{\sigma} \cdot (\vec{\nabla} \Delta) \times \vec{p} \right)$$

Off-diagonal spin-orbit and Darwin terms

What kind of effects should one look at?

Type 1: relativity provides correction to effect which exists non-relativistically

e.g.

- Cooper pair mass/London moment
- Shift in energy spectrum

Type 2: relativity produces effect which is not present non-relativistically

e.g.

- Dichroism
- SOC induced Josephson currents

What is circular dichroism?

$P^{L/R}(\omega)$ = power absorption of L/R circularly polarized light with frequency ω

The occurrence of $P(\omega) = P^L(\omega) - P^R(\omega) \neq 0$ is called circular dichroism.

Where is dichroism observed?

A: materials where parity is broken (sugar)

B: simulations where time-reversal symmetry is broken

1. either by an external magnetic field

2. or by an “internal” magnetic field

(due to ferromagnetic order)

type B dichroism is a relativistic effect.

Outline of the calculations:

unperturbed system: **inhomogeneous superconductor**

- described by Spin-Bogolubov-de Gennes equations

time-dependent perturbation: **polarized light**

- treated with golden rule for superconductors

stationary perturbations: **diagonal spin-orbit coupling**

off-diagonal spin-orbit

coupling

external magnetic field

- treated with 1st order stationary perturbation theory

Result:

power absorption in superconductors as
a function of

frequency

polarization

temperature

magnetic field

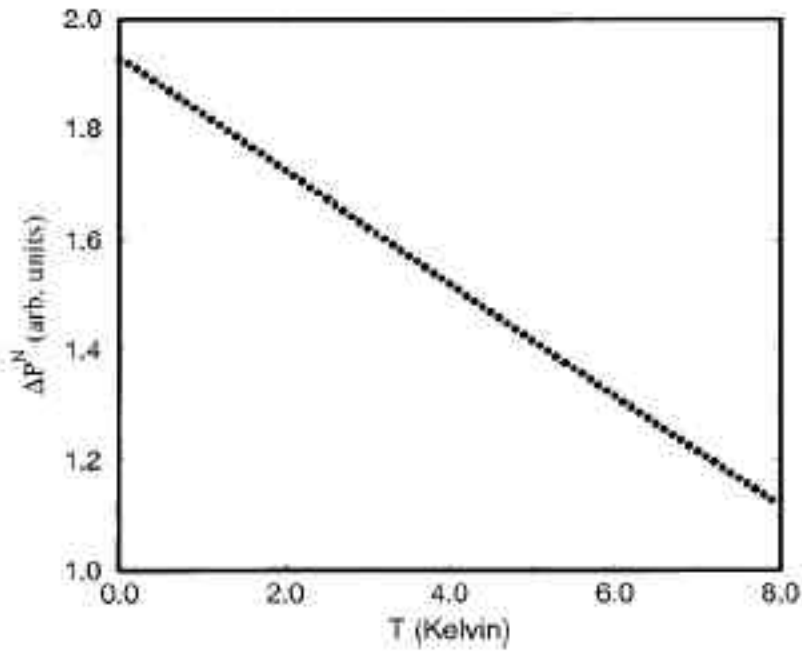


FIG. 1. Dichroism in the normal state vs temperature T . This and all other figures display only the contribution of SOC-induced dichroism. The other mechanisms are excluded from the calculation, as discussed in the main text. The numerical values of the parameters specifying the system are given in the main text.

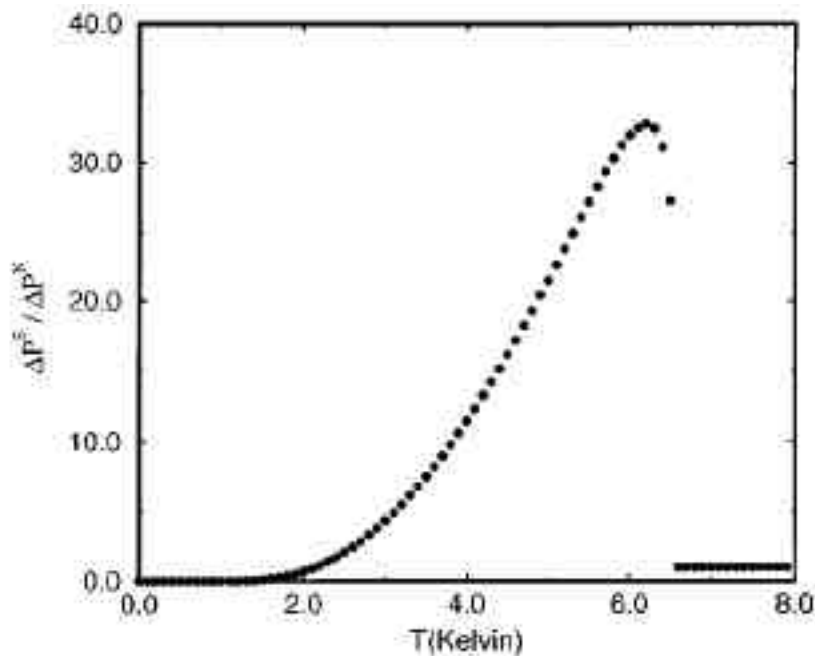


FIG. 2. Dichroism ratio vs T at small magnetic fields. A strong coherence peak is seen close to T_c , while near $T=0$ the curve approaches 0.

K. Capelle, E.K.U.G., B. L. Györfy, Phys.Rev. Lett. 78, 3753 (1997)

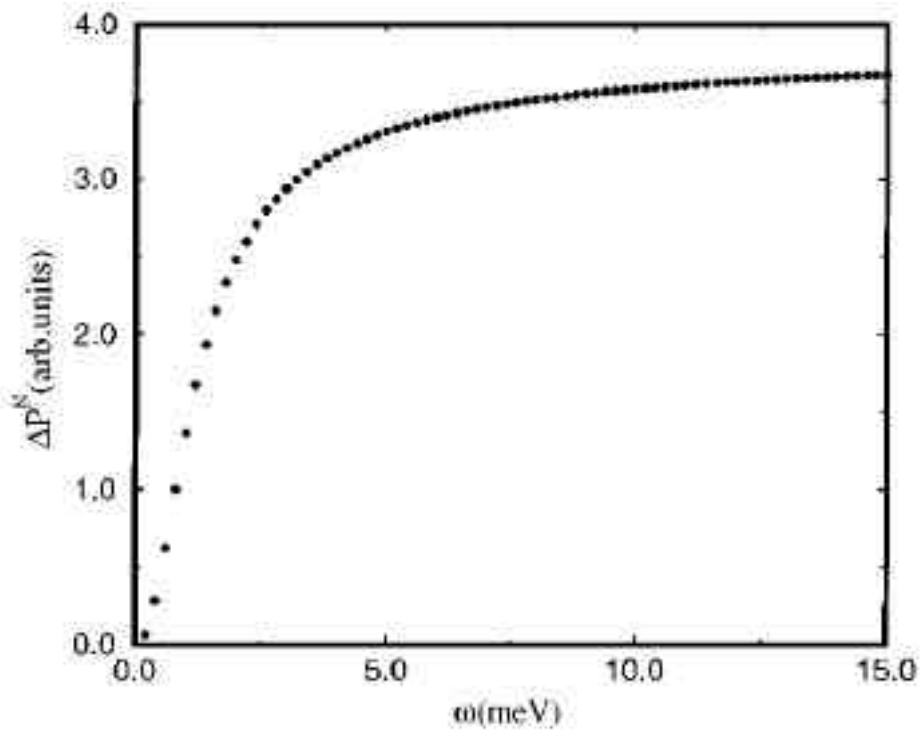


FIG. 7. Dichroism in the normal state vs frequency ω .

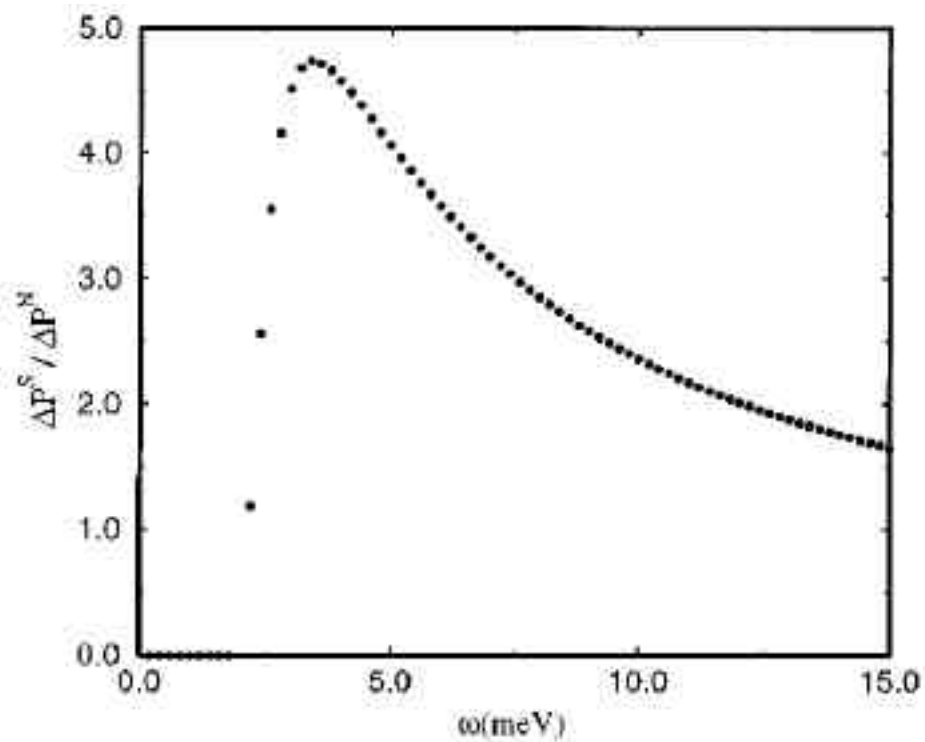


FIG. 8. Dichroism ratio vs ω . The absorption edge at $\omega=2\Delta$ has a mixed type I-II character, reflecting the behavior of the perturbations under time reversal.

K. Capelle, E.K.U.G., B. L. Györfy, Phys.Rev. Lett. 78, 3753 (1997)

Further details on the relativistic framework

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Further details on dichroism in superconductors

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