Ab initio pseudopotential calculations of the orbital magnetization

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Outline

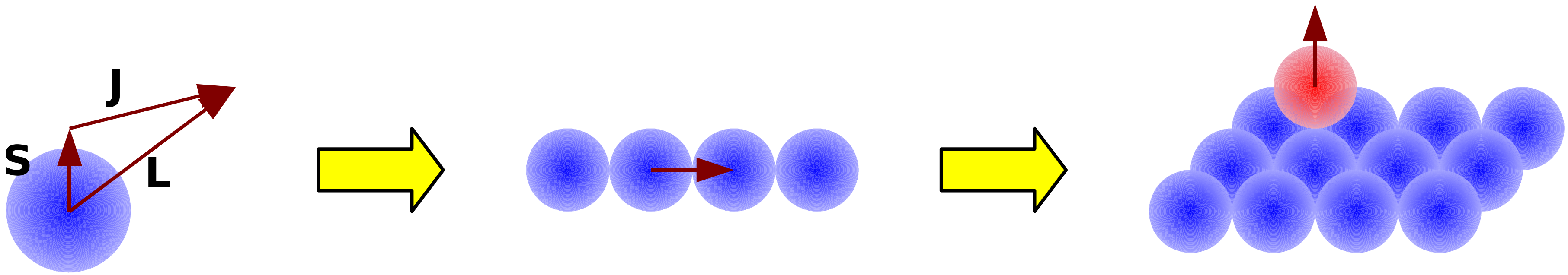
- Modern Theory of the orbital magnetization
- Application: EPR g-tensor in molecules and solids
- Orbital magnetization of Fe, Co and Ni
- Conclusions

Orbital magnetization

- Two contributions to the total magnetization

$$\mathbf{M}_{\mathrm{tot}} = \mathbf{M}_{\mathrm{spin}} + \mathbf{M}_{\mathrm{orb}}$$

- Orbital magnetization usually small in solids ...



- ... but *unquenched* in nanostructures

☞ Spin-Orbit interaction

Spin-orbit

Origin of M_{orb} in solid and molecules

$$\mathcal{H} = \frac{1}{2}\mathbf{p}^2 + V(\mathbf{r}) + \Delta\mathcal{H}_{\text{Z}} + \Delta\mathcal{H}_{\text{SO}} + \cdots$$

spin-other-orbit (SOO)
+
relativistic mass
corrections
+
...

Zeeman term

$$\Delta\mathcal{H}_{\text{Z}} = -\frac{\alpha\, g_e}{2}\mathbf{S}\cdot\mathbf{B}$$

SO term

$$\Delta\mathcal{H}_{\text{SO}} = \frac{\alpha^2\, g'}{4}\mathbf{S}\cdot[\nabla V(\mathbf{r})\times\mathbf{p}]$$

Atomic units,

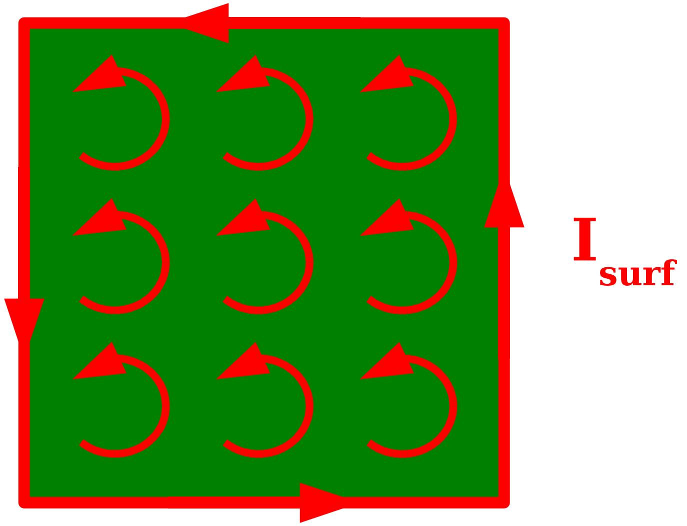
$$\alpha = 1/c$$
$$g' = 2(g_e - 1)$$

- molecule radicals
- paramagnetic defects in solids
- ferromagnetic metals

Schrekenbach and Ziegler, J. Phys. Chem. A **101**, 3388 (1997)

Definition

$$\mathbf{M}_{\mathrm{orb}} = \frac{1}{2c} \int \mathbf{r} \times \boldsymbol{j}(\mathbf{r})\, d\mathbf{r}$$

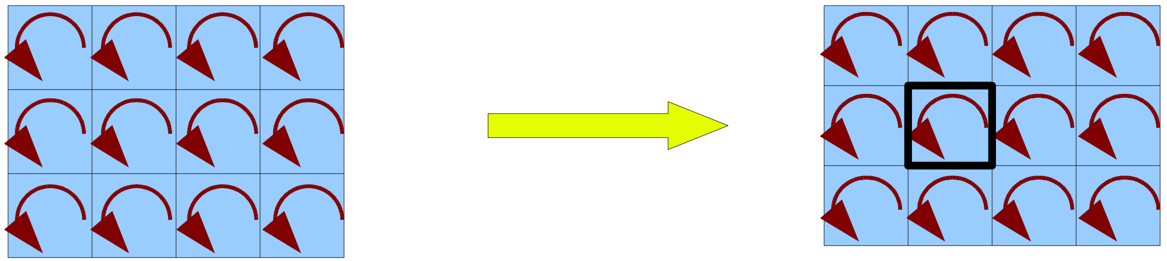


- Well defined in finite systems!
- Problems with periodic systems
  - position operator **r** incompatible with PBCs
  - surface currents

☞ 1990's: Modern Theory of Polarization

Periodic systems

Pass to Wannier functions



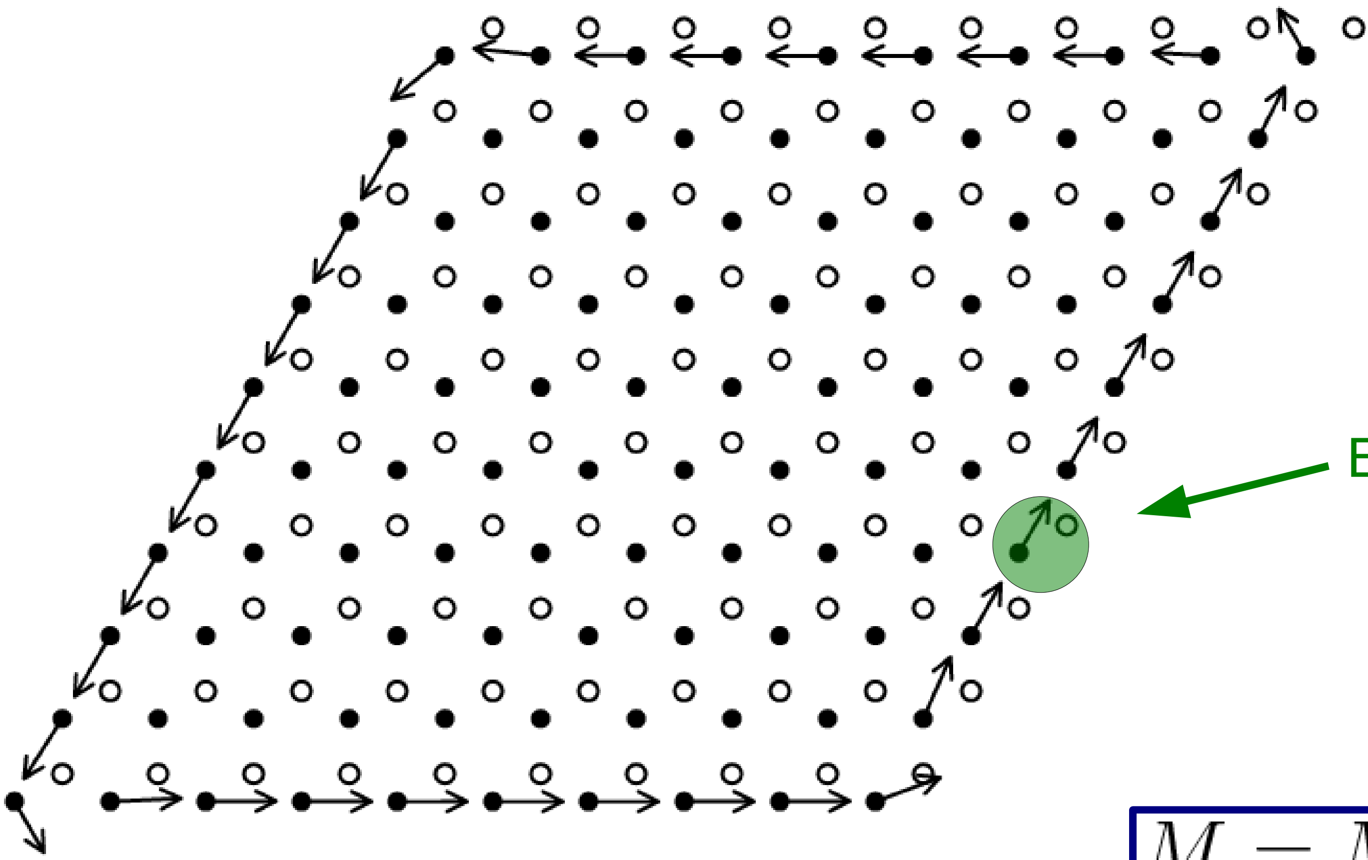
$$|\phi_n\rangle \qquad\qquad |\mathbf{R}n\rangle$$

Evaluate "Local Circulation" of the Wannier orbital

$$M_{\mathrm{LC}} = \frac{1}{2c}\sum_n \langle \mathbf{R}n|\mathbf{r}\times\mathbf{v}|\mathbf{R}n\rangle$$

What about surfaces?

Surface WFs



Each surface WF carries a net current!

$$\boxed{M = M_{\mathrm{LC}} + M_{\mathrm{IC}}}$$

Thonhauser, Ceresoli, Vanderbilt, Resta, PRL 95, 137205 (2005)
Ceresoli, Thohauser, Vanderbilt, Resta, PRB 74, 024408 (2006)

Periodic systems

$$\boxed{\mathbf{M}_{\mathrm{orb}} = \frac{\alpha}{2}\mathrm{Im}\sum_{n\mathbf{k}} f_{n\mathbf{k}} \left\langle \partial_{\mathbf{k}} u_{n\mathbf{k}} \right| \times \left(H_{\mathbf{k}} + E_{n\mathbf{k}} - 2\mu \right) \left| \partial_{\mathbf{k}} u_{n\mathbf{k}} \right\rangle}$$

- Derived independently by two groups (2005-2006)
  Ceresoli, Resta, Thonhauser, Vanderbilt
  Xiao, Yao, Fang, Shi, Vignale, Niu
- Valid for insulators and metals
- Easy to implement in all-electron (AE) electronic structure codes
- Extra terms for pseudopotentials (PS)

$$\mathbf{M}_{\mathrm{orb}}^{\mathrm{PS}} = \mathbf{M}'_{\mathrm{orb}} + \Delta\mathbf{M}_{\mathrm{PS}}$$

GIPAW

Origin of extra terms: NLPP's coupling to EM fields [1,2]

Correct recipe: Gauge Including Projector Augmented Wave [3]

- Gauge invariant, AE and PS eigenvalues coincide
- Reconstruct the AE wvfcs from PS wvfcs
- Based on the PAW method [4]

$$\langle \psi_{\mathrm{ae}} | \mathcal{O} | \psi_{\mathrm{ae}} \rangle \equiv \langle \psi_{\mathrm{ps}} | \overline{\mathcal{O}} | \psi_{\mathrm{ps}} \rangle = \langle \psi_{\mathrm{ps}} | \mathcal{O} + \Delta\mathcal{O} | \psi_{\mathrm{ps}} \rangle$$

[1] Ismail-Beigi, Chang and Louie, PRL **87**, 087402 (2001)
[2] Pickard and Mauri, PRL **91**, 196401 (2003)
[3] Pickard and Mauri, PRB **63**, 245101 (2001)
[4] Blöchl, PRB **50**, 17953 (1994)

GIPAW transformation

projector **AE atomic**

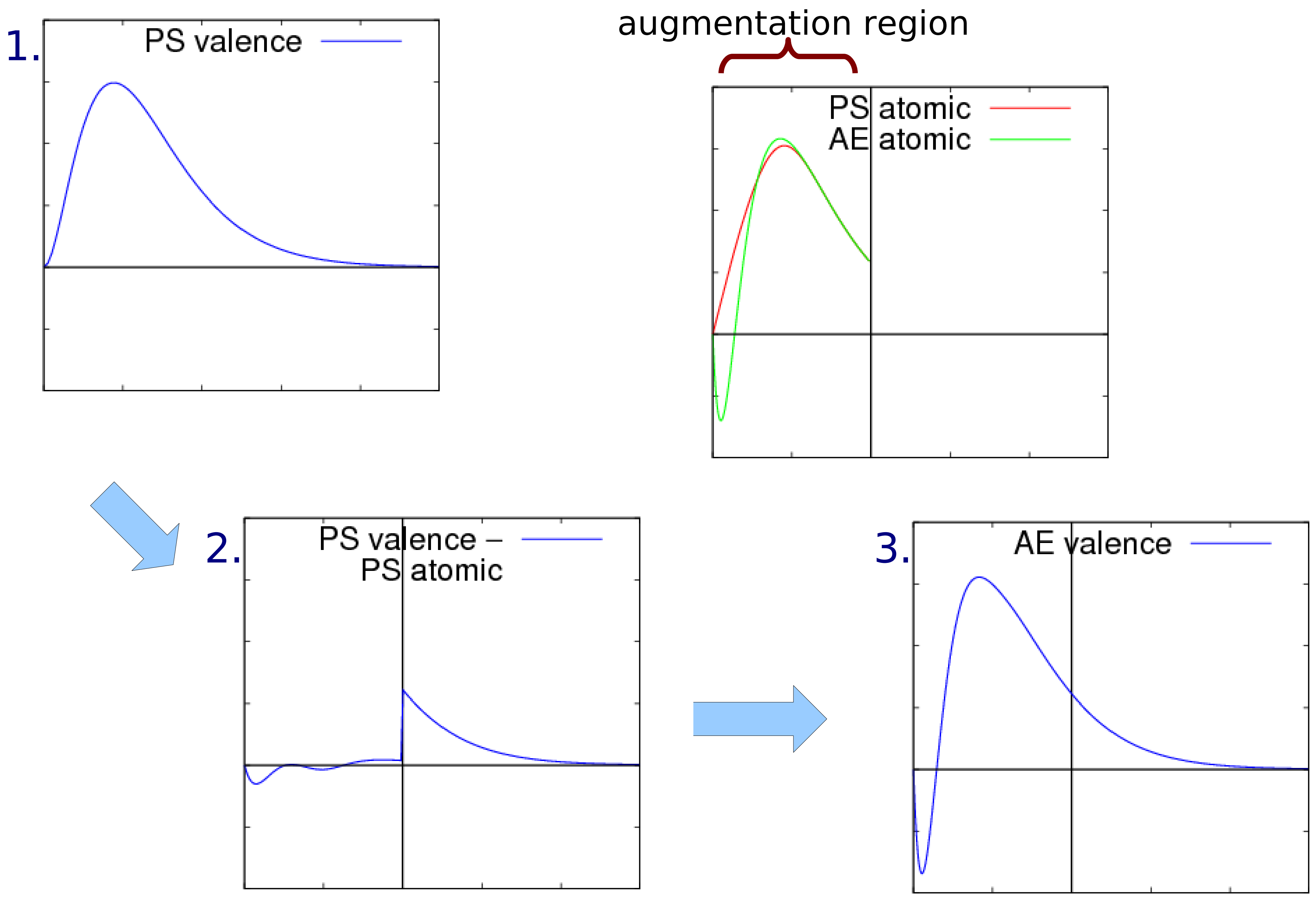
$$\Delta\mathcal{O} = \sum_{\mathbf{R},nm} e^{\frac{i\alpha}{2}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} \, |\widetilde{p}_{\mathbf{R},n}\rangle \left[\langle\phi_{Rn}|\widehat{\mathcal{O}}|\phi_{Rm}\rangle - \langle\widetilde{\phi}_{Rn}|\widehat{\mathcal{O}}|\widetilde{\phi}_{Rm}\rangle \right] \langle\widetilde{p}_{\mathbf{R},m}| \, e^{-\frac{i\alpha}{2}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

PS atomic **projector**

Inner operator

$$\widehat{\mathcal{O}} = e^{-\frac{i\alpha}{2}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}} \, \mathcal{O} \, e^{\frac{i\alpha}{2}\mathbf{r}\cdot\mathbf{R}\times\mathbf{B}}$$

GIPAW reconstruction



Orbital magnetization

$$\boxed{\mathbf{M} = \mathbf{M}' + \Delta\mathbf{M}_{\mathrm{bare}} + \Delta\mathbf{M}_{\mathrm{para}} + \Delta\mathbf{M}_{\mathrm{dia}}}$$

$$\mathbf{M}' = \frac{\alpha}{2}\mathrm{Im}\sum_{n\mathbf{k}} f_{n\mathbf{k}} \langle \partial_{\mathbf{k}} u_{n\mathbf{k}} | \times (H_{\mathbf{k}} + E_{n\mathbf{k}} - 2\mu) | \partial_{\mathbf{k}} u_{n\mathbf{k}} \rangle$$

$$\Delta\mathbf{M}_{\mathrm{bare}} = \frac{\alpha}{2}\sum_{\mathbf{R}} \left\langle (\mathbf{R}-\mathbf{r}) \times \frac{1}{i}\left[\mathbf{r}-\mathbf{R}, V_R^{\mathrm{NL}}\right] \right\rangle$$

$$\Delta\mathbf{M}_{\mathrm{para}} = \frac{\lambda\alpha}{2}\sum_{\mathbf{R}} \left\langle (\mathbf{R}-\mathbf{r}) \times \frac{1}{i}\left[\mathbf{r}-\mathbf{R}, F_R^{\mathrm{NL}}\right] \right\rangle$$

$$\Delta\mathbf{M}_{\mathrm{dia}} = \frac{\lambda\alpha^2}{2}\sum_{\mathbf{R}} \langle \boldsymbol{E}_R^{\mathrm{NL}} \rangle$$

All quantities calculated with PS hamiltonian and wavefunctions!

$\lambda = g'/8$

Reconstruction terms

Paramagnetic term

$$F_R^{\mathrm{NL}} = \sum_{\mathbf{R},nm} |\widetilde{p}_{\mathbf{R},n}\rangle\, f_{\mathbf{R},nm}\, \langle\widetilde{p}_{\mathbf{R},m}|$$

$$f_{\mathbf{R},nm} = \langle\phi_{\mathbf{R},n}|\underbrace{\boldsymbol{\sigma}\cdot\nabla V^{\mathrm{AE}}\times\mathbf{p}}_{\frac{2}{r}\frac{dV(r)}{dr}\mathbf{S}\cdot\mathbf{L}}|\phi_{\mathbf{R},m}\rangle - \langle\widetilde{\phi}_{\mathbf{R},n}|\boldsymbol{\sigma}\cdot\nabla V^{\mathrm{loc}}\times\mathbf{p}|\widetilde{\phi}_{\mathbf{R},m}\rangle$$

Diamagnetic term

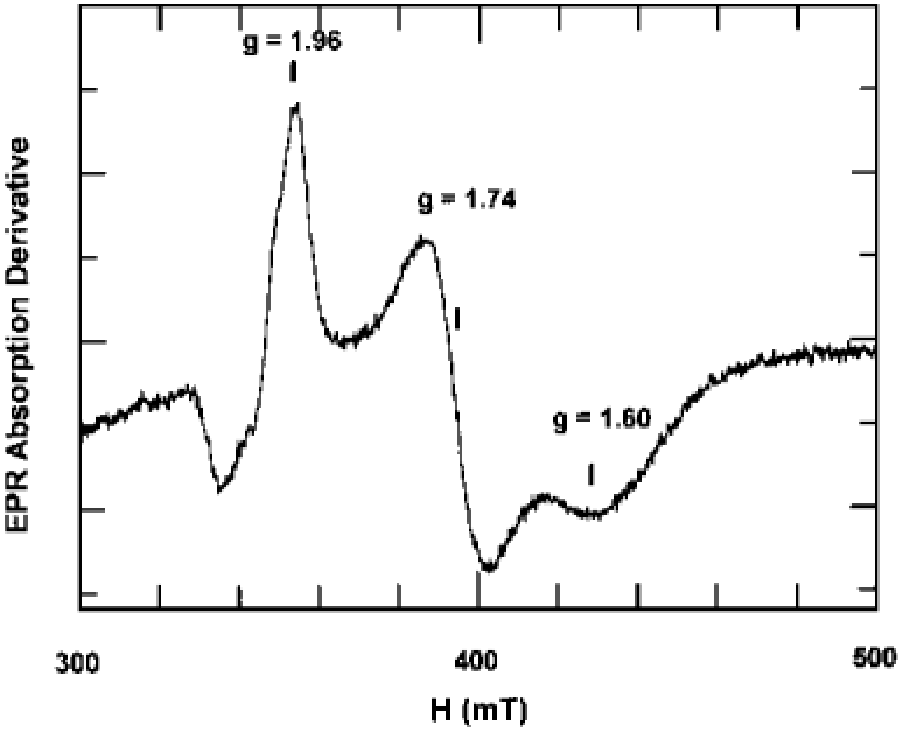
$$\boldsymbol{E}_R^{\mathrm{NL}} = \sum_{\mathbf{R},nm} |\widetilde{p}_{\mathbf{R},n}\rangle\, \mathbf{e}_{\mathbf{R},nm}\, \langle\widetilde{p}_{\mathbf{R},m}|$$

$$\mathbf{e}_{\mathbf{R},nm} = \langle\phi_{\mathbf{R},n}|\mathbf{r}\times(\boldsymbol{\sigma}\times\nabla V^{\mathrm{AE}})|\phi_{\mathbf{R},m}\rangle - \langle\widetilde{\phi}_{\mathbf{R},n}|\mathbf{r}\times(\boldsymbol{\sigma}\times\nabla V^{\mathrm{loc}})|\widetilde{\phi}_{\mathbf{R},m}\rangle$$

same as in: Pickard and Mauri, PRL **88**, 086403 (2002)

EPR spectroscopy

EPR = Electron Paramagnetic Resonance

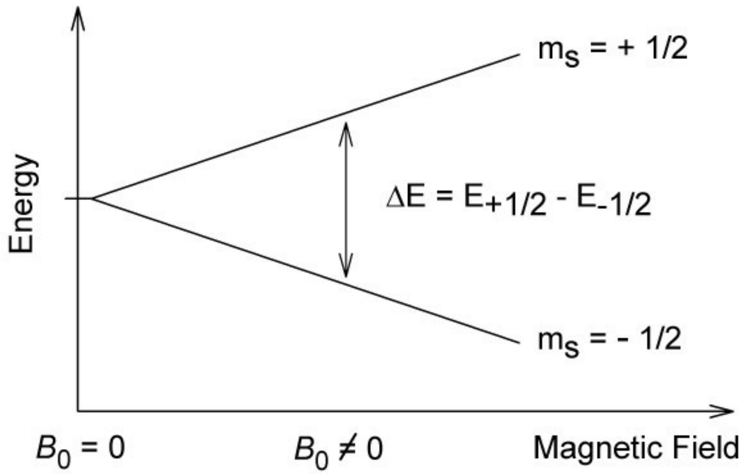


- Paramagnetic defects in solids
- g-tensor and hyperfine couplings very sensitive to chemical environment

Tipical fields	~0.5 T
Resonance	~14 GHz

Connection to the orbital magn.

For a spin 1/2



$$E = \frac{\alpha}{2}\, g\, m_S\, B$$

"chemical shift"

The g factor is

$$g = \frac{2}{\alpha}\frac{\partial \Delta E}{\partial B} = \frac{2}{\alpha}\Delta M_{\mathrm{tot}} = g_e + \underbrace{\frac{2}{\alpha}\Delta M_{\mathrm{orb}}}_{\Delta g_{\mathrm{SO}}}$$

2.002319...

Calculation of the g-tensor

- non perturbative method, SO interactions to all orders
- 3 SCF calculations (*j* = 1..3) including SO
- Δg_{SO} directly from $\boldsymbol{M}_{orb}$

$$\Delta g_{\mathrm{SO}}^{ij} = \frac{2}{\alpha}\left[\mathbf{M}_{\mathrm{orb}}^{i}(\mathbf{S} = \uparrow_j) - \mathbf{M}_{\mathrm{orb}}^{i}(\mathbf{S} = \downarrow_j)\right]$$

Linear response (LR) method

Linearizing Δg_{SO} with respect to SO coupling strenght

$$\Delta \overleftrightarrow{g}_{\mathrm{SO}} = -\alpha\, g' \sum_{S=\pm 1/2} \mathbf{S} \cdot \int d\mathbf{r}'\, \nabla V(\mathbf{r}') \times \overleftrightarrow{j}^{(1)}_{S}(\mathbf{r}')$$

Current induced by
uniform magnetic field

- SCF calculation (no SO included)
- LR with respect to uniform **B** (3 pertubations)
- Δg_{SO} from induced current

Pickard and Mauri, PRL **88**, 086403 (2002)

Technical details

- 8000 Å^3 Cubic supercell
- 100 Ry PW cutoff
- PBE functional
- 2x2x2 k-points
- Norm conserving PPs
- 2 GIPAW projectors x angular momentum channel
- *du/d***k** computed as a covariant derivate

Linear response

- GIPAW linear response (LR) recently implemented in quantum-Espresso by Ceresoli, Seitsonen and Gerstmann
- Available for production in Espresso-4.0
- Capabilities
  - Magnetic susceptibility
  - NMR shielding tensors
  - Electric Field Gradients (EFGs)
  - EPR g-tensor
  - Hyperfine couplings
  - XAS (under development, S. Fabris and Y. Yao)
  - XANES (under development, G. Gougoussis and M. Calandra)

References and codes:

- www.gipaw.net
- www.quantum-espresso.org

Results for diatomic radicals

Molecule		Expt.	LR	This work
H_2^+	$\Delta g_{\parallel}$	N/A	-39.2	-39.2
	$\Delta g_{\perp}$	N/A	-41.7	-42.1
CN	$\Delta g_{\parallel}$	N/A	-141	-134
	$\Delta g_{\perp}$	-2000	-2600	-2607
CO^+	$\Delta g_{\parallel}$	N/A	-136	-141
	$\Delta g_{\perp}$	-2400	-3229	-3222
BO	$\Delta g_{\parallel}$	-800	-70	-75
	$\Delta g_{\perp}$	-1100	-2382	-2391
BS	$\Delta g_{\parallel}$	-700	-81	-68
	$\Delta g_{\perp}$	-8100	-9982	-10003
AlO	$\Delta g_{\parallel}$	-800	-149	-148
	$\Delta g_{\perp}$	-1900	-1852	-1841
KrF	$\Delta g_{\parallel}$	-2000	-360	-363
	$\Delta g_{\perp}$	66000	59920	58885
XeF	$\Delta g_{\parallel}$	-2800	-358	-360
	$\Delta g_{\perp}$	124000	163369	146558

- expt. data: solid matrix
- values in ppm
- SOO not included

Results for molecule radicals

Molecule		Expt.	LR	This work
H_2O^+	Δg_{xx}	200	-234	-225
	Δg_{yy}	18000	11972	12028
	Δg_{zz}	4800	4619	4650
NO_2	Δg_{xx}	3900	4878	4807
	Δg_{yy}	-11300	-14230	-14327
	Δg_{zz}	-300	-810	-826
NF_2	Δg_{xx}	-100	-774	-785
	Δg_{yy}	6200	7393	7404
	Δg_{zz}	8800	4680	4684

- expt. data: solid matrix
- values in ppm
- SOO not included

GIPAW corrections

CN

	$\Delta g_{\|\|}$	$\Delta g_{\perp}$
M_{bare}	-2195	45
ΔM_{bare}	-234	6
ΔM_{para}	-4	-3
ΔM_{dia}	8	0
RMC[1]	-182	-182
Total	-2607	-134

H_2O^+

	Δg_{xx}	Δg_{yy}	Δg_{zz}
M_{bare}	31	11780	4894
ΔM_{bare}	-7	497	11
ΔM_{para}	-2	-2	-2
ΔM_{dia}	15	15	9
RMC[1]	-262	-262	-262
Total	-225	12028	4650

1. Relativistic Mass Corrections

$\Delta M_{\mathrm{bare}} \sim$ 5-10 %

Advantages over LR

- need only SCF calculations $\rightarrow$ LDA+U, EXX, OEP, B3LYP, ...
- no magnetic field
- no symmetry restrictions
- SO interaction to all orders

Work in progress

- benchmark against paramagnetic defects in solids
- speedup
- convergence w.r.t. k-points

Orbital magnetization in ferromagnets

Einstein only experiment!

http://www.ptb.de/en/publikationen/jahresberichte/jb2005/nachrdjahres/s23e.html

Einstein-de Haas effect

The effect corresponds to the **mechanical rotation** that is induced in a **ferromagnetic material** (of cylindrical shape and originally at rest), suspended with the aid of a thin string inside a coil, on **driving an impulse of electric current through the coil**. To this mechanical rotation of the ferromagnetic material (say, iron) is associated a mechanical angular momentum, which, by the law of conservation of angular momentum, must be compensated by an equally large and oppositely directed angular momentum inside the ferromagnetic material.

$$\begin{aligned} M_{\mathrm{tot}} &= (\alpha/2)\,(L + g_e\,S) \\ J_{\mathrm{tot}} &= L + S \end{aligned}$$

By measuring M_{tot} and J_{tot} you can extract S and L!

Orbital magnetization in metals

Which DFT is better for the orbital magnetization?

Previous calculations

- LDA and GGA underestimate M_{orb} [1,5]
- better agreement with orbital polarization (OP) [2,3,4]

$$\Delta\mathcal{H} = -B\,L\,\hat{L}_z$$

- ... and CDFT [3,4]
- [6] provides a link between CDFT and OP

[1] Singh, Callaway, Wang, PRB 14, 1214 (1976)
[2] Eriksson, Johanson, Albers, Boring, Brooks, PRB 42, 2707 (1990)
[3] Ebert, Battocletti, Solid State Commun. 98, 785 (1996)
[4] Ebert, Battocletti, Gross, Europhys. Lett. 40, 525 (1997)
[5] Sharma, Pittalis, Kurth, Shallcross, Dewhurst, Gross, PRB 76, 100401 (2007)
[6] Morbec, Capelle, Int. J. Quantum Chem., in press (2008)

Results for Fe, Co and Ni

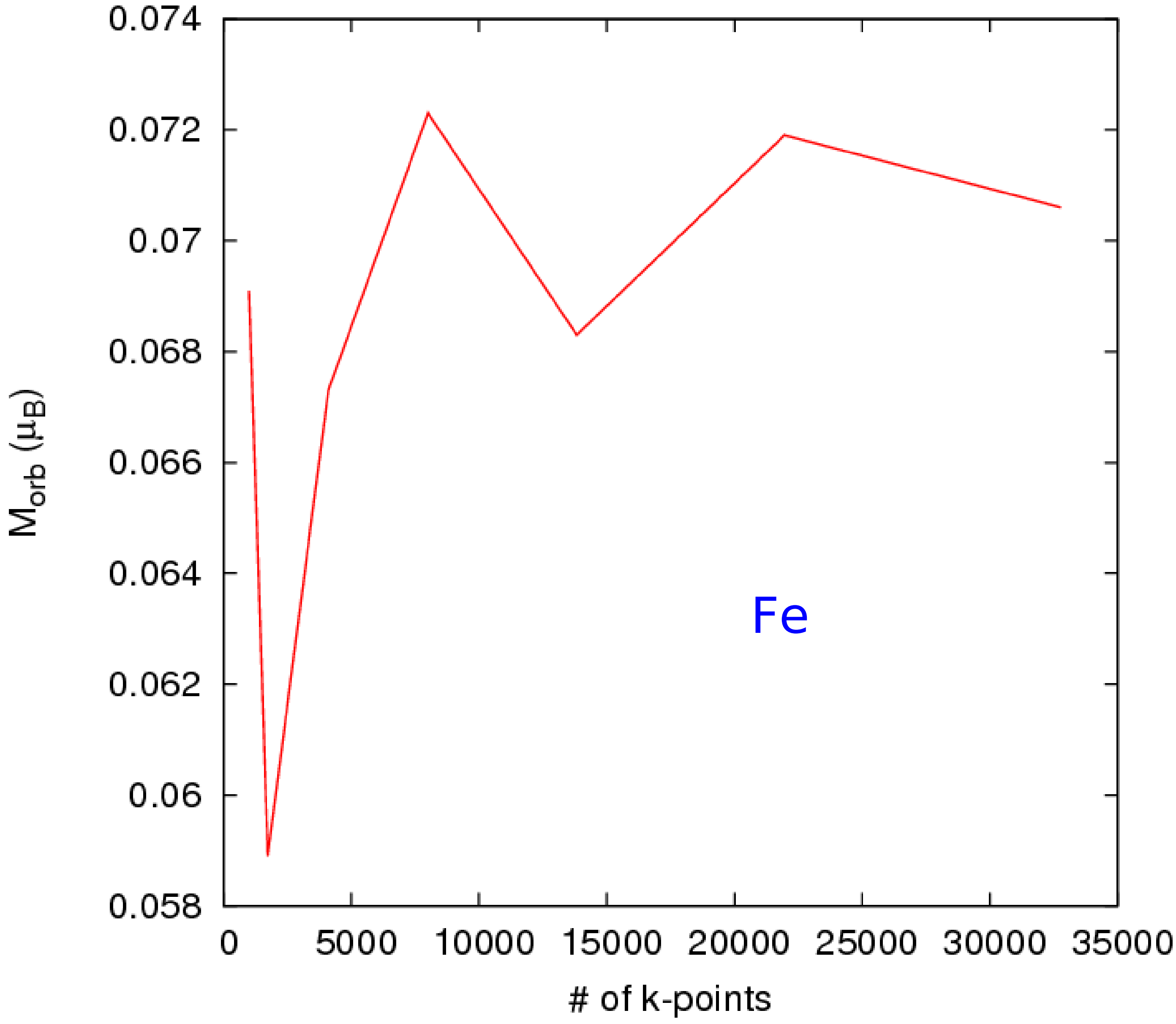
Method	Fe (bcc)	Co (hcp)	Ni (fcc)
LMTO LDA [2]	0.04	0.07	0.05
LMTO LDA+OP [2]	0.06	0.14	0.07
KKR LDA+OP [4]	0.083	0.120	0.051
KKR CDFT [4]	0.070	0.080	0.049
FLAPW LDA [5]	0.053	0.069	0.038
FLAPW GGA [5]	0.051	0.073	0.037
This work GGA	0.071	0.092	0.050
Expt. [7]	0.081	0.133	0.053

This work: PBE, 90 Ry, up to 32x32x32 k-points

all values in μ_B

[7] Meyer and Asch, J. Appl. Phys. 32, 330S (1961)

k-points convergence



Contributions to the magnetization

$$\mathbf{M} = \mathbf{M}' + \Delta\mathbf{M} = (\mathbf{M}_{\mathrm{LC}} + \mathbf{M}_{\mathrm{IC}}) + \Delta\mathbf{M}$$

	M_{orb}	M_{LC}	M_{IC}	ΔM
Fe (bcc)	0.0712	0.0883	−0.0172	0.0001
Co (hcp)	0.0917	0.1086	−0.0177	0.0008
Ni (fcc)	0.0504	0.0503	−0.0015	0.0016

all values in μ_B

Conclusions

- Derived orbital magnetization formula for ab initio *pseudopotential* calculations
- Non perturbative method to compute EPR g-tensor
  tested against small molecule radicals
- We computed the orbital magnetization of Fe, Co and Ni
- Work in progress
  - evaluate speedup with respect to linear response method
  - combine non perturbative EPR method and LDA+U

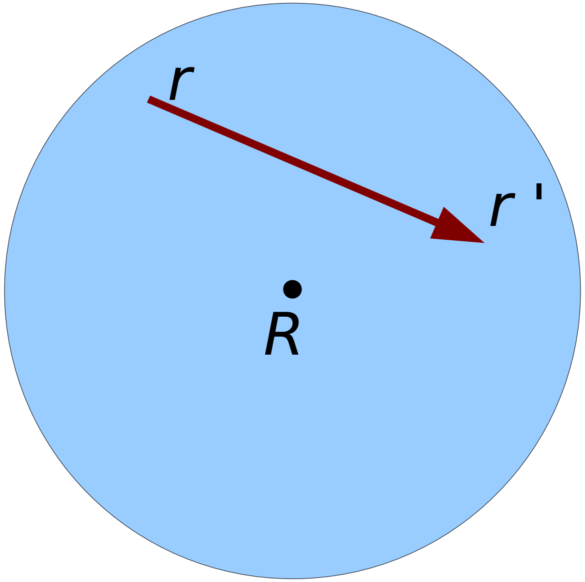
Extra slides

- Coupling to NLPPs (ICL)
- Coupling to NLPPs (Pickard-Mauri)
- Effective spin hamiltonian
- Spin-orbit

Non local pseudopotential

Magnetic field coupling to non local potentials

$$V_R^{\mathrm{NL}}(\mathbf{r},\mathbf{r}') \longrightarrow V_R^{\mathrm{NL}}(\mathbf{r},\mathbf{r}')\exp\left[i\alpha\int_{\mathbf{r}\rightarrow\mathbf{r}'}\mathbf{A}(\mathbf{s})\cdot d\mathbf{s}\right]$$



augmentation
region

- gauge invariant

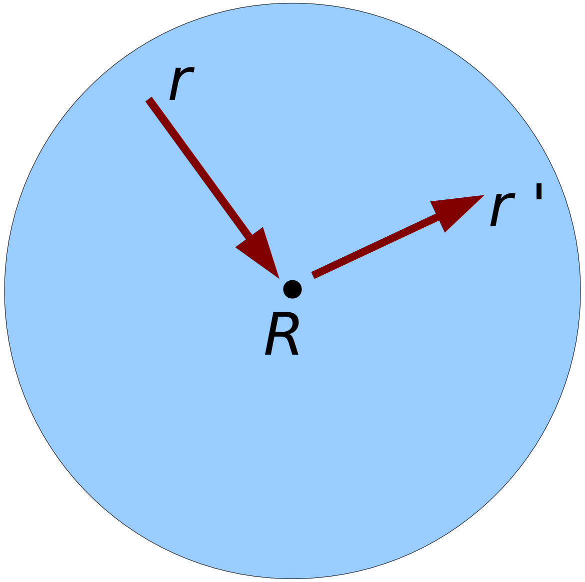
$$\mathbf{M} \equiv -\left\langle \frac{\partial \mathcal{H}_{\mathrm{PS}}}{\partial \mathbf{B}} \right\rangle = -\frac{\alpha}{2}\left\langle \mathbf{r}\times\mathbf{v}_{\mathrm{PS}}\right\rangle$$

Ismail-Beigi, Chang and Louie, PRL **87**, 087402 (2001)

Non local pseudopotentials

Magnetic field coupling to non local potentials

$$V_R^{\mathrm{NL}}(\mathbf{r},\mathbf{r}') \to V_R^{\mathrm{NL}}(\mathbf{r},\mathbf{r}') \exp\left[i\alpha \int_{\mathbf{r}\to\mathbf{R}\to\mathbf{r}'} \mathbf{A}(\mathbf{s})\cdot d\mathbf{s} \right]$$



augmentation region

- gauge invariant
- same AE and PS eigenvalues

$$\mathbf{M} \equiv -\left\langle \frac{\partial \mathcal{H}_{\mathrm{PS}}}{\partial \mathbf{B}} \right\rangle \neq -\frac{\alpha}{2} \langle \mathbf{r} \times \mathbf{v}_{\mathrm{PS}} \rangle$$

Pickard and Mauri, PRL **91**, 196401 (2003)

Effective spin hamiltonian

$$\mathcal{H}_{\text{eff}} = \frac{\alpha}{2}\mathbf{S} \cdot \overset{\leftrightarrow}{g} \cdot \mathbf{B} + \sum_R \mathbf{S} \cdot \overset{\leftrightarrow}{A}_R \cdot \mathbf{I}_R + \mathbf{S} \cdot \overset{\leftrightarrow}{D} \cdot \mathbf{S}$$

g tensor

hyperfine couplings

Zero field splitting

$$\overset{\leftrightarrow}{g} = g_e \overset{\leftrightarrow}{1} + \Delta \overset{\leftrightarrow}{g}_{\text{SO}} + \cdots$$ SOO + other relativistic

GIPAW

Gauge Including Projector Augmented Wave [1]

- Correct treatment of magnetic field coupling
- Gauge invariant
- AE and PS eigenvalues coincide
- Based on the PAW formalism [2]
- Yields accurate AE properties from PS wavefunctions

$$\langle\psi_{\mathrm{ae}}|\mathcal{O}|\psi_{\mathrm{ae}}\rangle \equiv \langle\psi_{\mathrm{ps}}|\overline{\mathcal{O}}|\psi_{\mathrm{ps}}\rangle = \langle\psi_{\mathrm{ps}}|\mathcal{O} + \Delta\mathcal{O}|\psi_{\mathrm{ps}}\rangle$$

[1] Pickard and Mauri, PRB **63**, 245101 (2001)
[2] Blöchl, PRB **50**, 17953 (1994)

Technical details

- Norm conserving PPs
- 90 Ry PW cutoff, 0.001 Ry cold smearing
- PBE functional
- 2 GIPAW projectors x angular momentum channel
- *du/d***k** computed via **k·p** method
- up to 32x32x32 k-points
- spin constrained along easy axis (Fe [100], Ni [111], Co [001])

Periodic systems

$$\boxed{\mathbf{M} = \mathbf{M}' + \Delta\mathbf{M}_{\mathrm{bare}} + \Delta\mathbf{M}_{\mathrm{para}} + \Delta\mathbf{M}_{\mathrm{dia}}}$$

$$\mathbf{M}' = \frac{\alpha}{2}\mathrm{Im}\sum_{n\mathbf{k}} f_{n\mathbf{k}} \left\langle \partial_{\mathbf{k}} u_{n\mathbf{k}} \right| \times \left(H_{\mathbf{k}} + E_{n\mathbf{k}} - 2\mu \right) \left| \partial_{\mathbf{k}} u_{n\mathbf{k}} \right\rangle$$

$$\Delta\mathbf{M}_{\mathrm{bare}} = \frac{\alpha}{2} \sum_{n\mathbf{k}\sigma}^{\mathrm{occ}} \sum_{\tau,ij} \left\langle u_{n\mathbf{k}\sigma} \middle| \partial_{\mathbf{k}} \beta^{\mathbf{k}}_{\tau,i} \right\rangle \times v^{\tau}_{ij} \left\langle \partial_{\mathbf{k}} \beta^{\mathbf{k}}_{\tau,j} \middle| u_{n\mathbf{k}\sigma} \right\rangle$$

$$\Delta\mathbf{M}_{\mathrm{para}} = \frac{\lambda\alpha}{2} \sum_{n\mathbf{k}\sigma}^{\mathrm{occ}} \sum_{\tau,ij} \left\langle u_{n\mathbf{k}\sigma} \middle| \partial_{\mathbf{k}} \widetilde{p}^{\mathbf{k}}_{\tau,i} \right\rangle \times f^{\tau}_{ij} \left\langle \partial_{\mathbf{k}} \widetilde{p}^{\mathbf{k}}_{\tau,j} \middle| u_{n\mathbf{k}\sigma} \right\rangle$$

$$\Delta\mathbf{M}_{\mathrm{dia}} = \frac{\lambda\alpha^2}{2} \sum_{n\mathbf{k}\sigma}^{\mathrm{occ}} \sum_{\tau,ij} \left\langle u_{n\mathbf{k}\sigma} \middle| \widetilde{p}^{\mathbf{k}}_{\tau,i} \right\rangle \mathbf{e}^{\tau}_{ij} \left\langle \widetilde{p}^{\mathbf{k}}_{\tau,j} \middle| u_{n\mathbf{k}\sigma} \right\rangle$$