# The $Xe_3^+$ mystery: an Octopus story

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# In the beginning...

**r1**

```
2001-12-04 03:51

  * [r1] .: New repository initialized by cvs2svn.
```

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# In the beginning...

## r2

```
2001-12-04 03:51  marques

  * [r2] src, src/Makefile, src/asinh.F90, src/atom.F90,
    src/config.h, src/fdf.F90, src/global.F90, src/kb.F90,
    src/main.F90, src/math.F90, src/mesh.F90, src/ps.F90,
    src/run.F90, src/specie.F90, src/spline.F90, src/systm.F90,
    src/units.F90, src/xc_old.F90:

    Very preliminary version of new tddft code now
    baptized octopus ;))
```

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# Noncollinear magnetism

## r178

```
2002-05-29 13:16  marques

  * [r178] configure, configure.ac, src/eigen_cg1.F90,
    src/h_inc.F90, src/scf.F90, src/states.F90,
    src/xc_pot.F90:

    Code merge - a couple of new things on non-collinear spin
    (still doesn't converge), and a couple of bug fixes.
```

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# Noncollinear magnetism

- Wavefunctions are two-component spinors:

$$\Psi(\boldsymbol{r}) \equiv \left(\psi^{\uparrow}(\boldsymbol{r}),\ \psi^{\downarrow}(\boldsymbol{r})\right); \qquad \rho^{\alpha\beta}(\boldsymbol{r}) = \sum_i f_i \psi_i^{\alpha}(\boldsymbol{r}) \psi_i^{*\beta}(\boldsymbol{r})$$

$$n(\vec{r}) = \rho^{\uparrow\uparrow}(\vec{r}) + \rho^{\downarrow\downarrow}(\vec{r})$$

- The direction of the magnetization density can vary over space:

$$\boldsymbol{m}(\boldsymbol{r}) = \left(2\mathfrak{Re}\left\{\rho^{\uparrow\downarrow}(\boldsymbol{r})\right\}, \quad -2\mathfrak{Im}\left\{\rho^{\uparrow\downarrow}(\boldsymbol{r})\right\}, \quad \rho^{\uparrow\uparrow}(\boldsymbol{r}) - \rho^{\downarrow\downarrow}(\boldsymbol{r})\right)$$

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# Noncollinear magnetism

The calculation of $v_{\rm xc}$ requires two extra steps:

- Transform the density matrix so that it is diagonal at each point:

$$\tilde{\rho}(\boldsymbol{r}) = U^{\dagger}(\boldsymbol{r}) \begin{pmatrix} \rho^{\uparrow\uparrow}(\boldsymbol{r}) & \rho^{\uparrow\downarrow}(\boldsymbol{r}) \\ \rho^{\downarrow\uparrow}(\boldsymbol{r}) & \rho^{\downarrow\downarrow}(\boldsymbol{r}) \end{pmatrix} U(\boldsymbol{r}) = \begin{pmatrix} \tilde{\rho}^{\uparrow}(\boldsymbol{r}) & 0 \\ 0 & \tilde{\rho}^{\downarrow}(\boldsymbol{r}) \end{pmatrix}$$

- Rotate the xc vector matrix back to the original reference frame:

$$v_{\rm xc}(\boldsymbol{r}) = U^{\dagger}(\boldsymbol{r}) \begin{pmatrix} \tilde{v_{\rm xc}}^{\uparrow}(\boldsymbol{r}) & 0 \\ 0 & \tilde{v_{xc}}^{\downarrow}(\boldsymbol{r}) \end{pmatrix} U(\boldsymbol{r}) = \begin{pmatrix} v_{\rm xc}^{\uparrow\uparrow}(\boldsymbol{r}) & v_{\rm xc}^{\uparrow\downarrow}(\boldsymbol{r}) \\ v_{\rm xc}^{\downarrow\uparrow}(\boldsymbol{r}) & v_{\rm xc}^{\downarrow\downarrow}(\boldsymbol{r}) \end{pmatrix}$$

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# Spin-orbit coupling

## r273

```
2002-11-18 02:31  acastro

  * [r273] src/atom.F90, src/h_external_pot.F90, src/h_so.F90,
    src/ps3D.F90:

    OK, after several hours and four beers from previous commit,
    I think I have a pretty definitive version of SO. The
    gradient is moved from the wavefuntion to the projector,
    thus speeding the code to almost a factor of two. The price
    to pay is that I think only I would be able to understand
    the code I wrote. But now calculations with SO are almost
    as fast as without it.

    Pretty productive night, but I am running out of beers.
```

# Spin-orbit coupling

Non-relativistic pseudopotentials in semi-local form:

$$\hat{v}^{\mathrm{SL}} = \sum_{lm} |Y_{lm}\rangle \, v_l(r) \, \langle Y_{lm}|$$

Relativistic pseudopotentials in semi-local form:

$$\hat{v}^{\mathrm{SL}} = \sum_{lm} |Y_{lm}\rangle \left[ v_l^{\mathrm{Avg}}(r) + v_l^{\mathrm{SO}} \mathbf{L} \cdot \mathbf{S} \right] \langle Y_{lm}|$$

$$v_l^{\mathrm{Avg}} = \frac{l}{2l+1} \left[ (l+1) v_{l+1/2} + l \, v_{l-1/2} \right]$$

$$v_l^{\mathrm{SO}} = \frac{1}{2l+1} \left[ v_{l+1/2} - v_{l-1/2} \right]$$

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# Spin-orbit coupling

Non-relativistic Kleinman and Bylander form:

$$\hat{v}^{\mathrm{KB}} = v_{\mathrm{loc}} + \sum_{l,m} \frac{|\psi_{l,m}\delta v_l\rangle\langle\psi_{l,m}\delta v_l|}{\langle\psi_{l,m}|\delta v_l|\psi_{l,m}\rangle} \qquad \delta v_l = v_l - v_{\mathrm{loc}}$$

Octopus implementation of relativistic Kleinman and Bylander form:

$$\hat{v}^{\mathrm{KB}} = v_{\mathrm{loc}} + \sum_{l,m} \frac{|\psi_{l,m}\delta v_l\rangle\langle\psi_{l,m}\delta v_l|}{\langle\psi_{l,m}|\delta v_l|\psi_{l,m}\rangle} \qquad \delta v_l = v_l^{\mathrm{Avg}} - v_{\mathrm{loc}}$$

$$+ \sum_{l,m} \frac{|\psi_{l,m}v_l^{\mathrm{SO}}\rangle\mathbf{L}\cdot\mathbf{S}\langle\psi_{l,m}v_l^{\mathrm{SO}}|}{\langle\psi_{l,m}|v_l^{\mathrm{SO}}|\psi_{l,m}\rangle}$$

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# A simple test case: cationic xenon clusters

## r273

```
2002-11-15 17:15  marques

  * [r266] share/PP/TM2/Ar.ascii, share/PP/TM2/Ne.ascii,
    share/PP/TM2/Xe.ascii:

    Added Ne, Ar and Xe Troullier-Martins pseudopotential.
```

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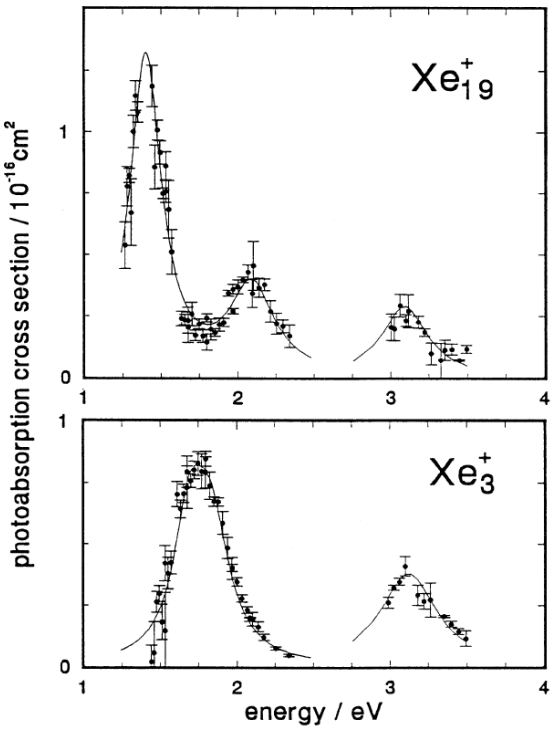
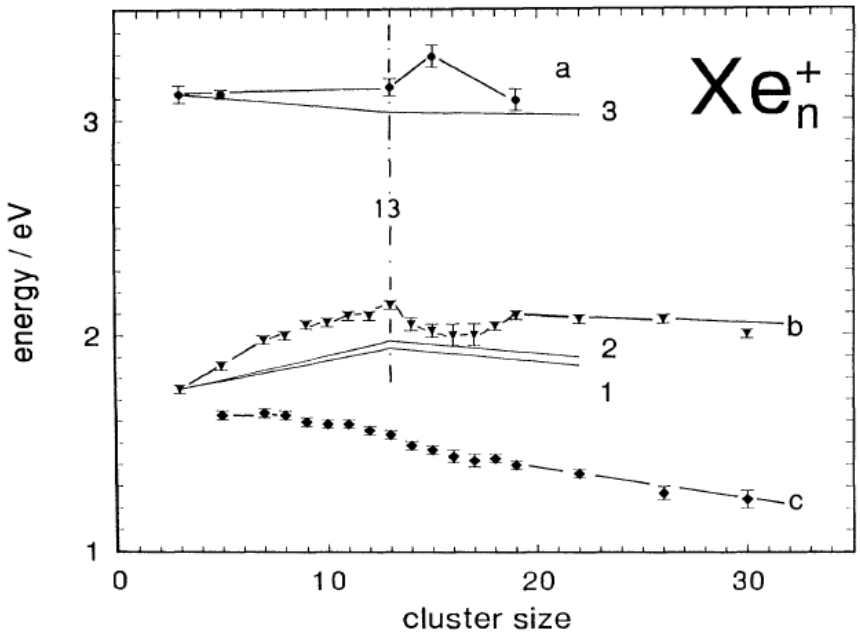
# A simple test case: cationic xenon clusters

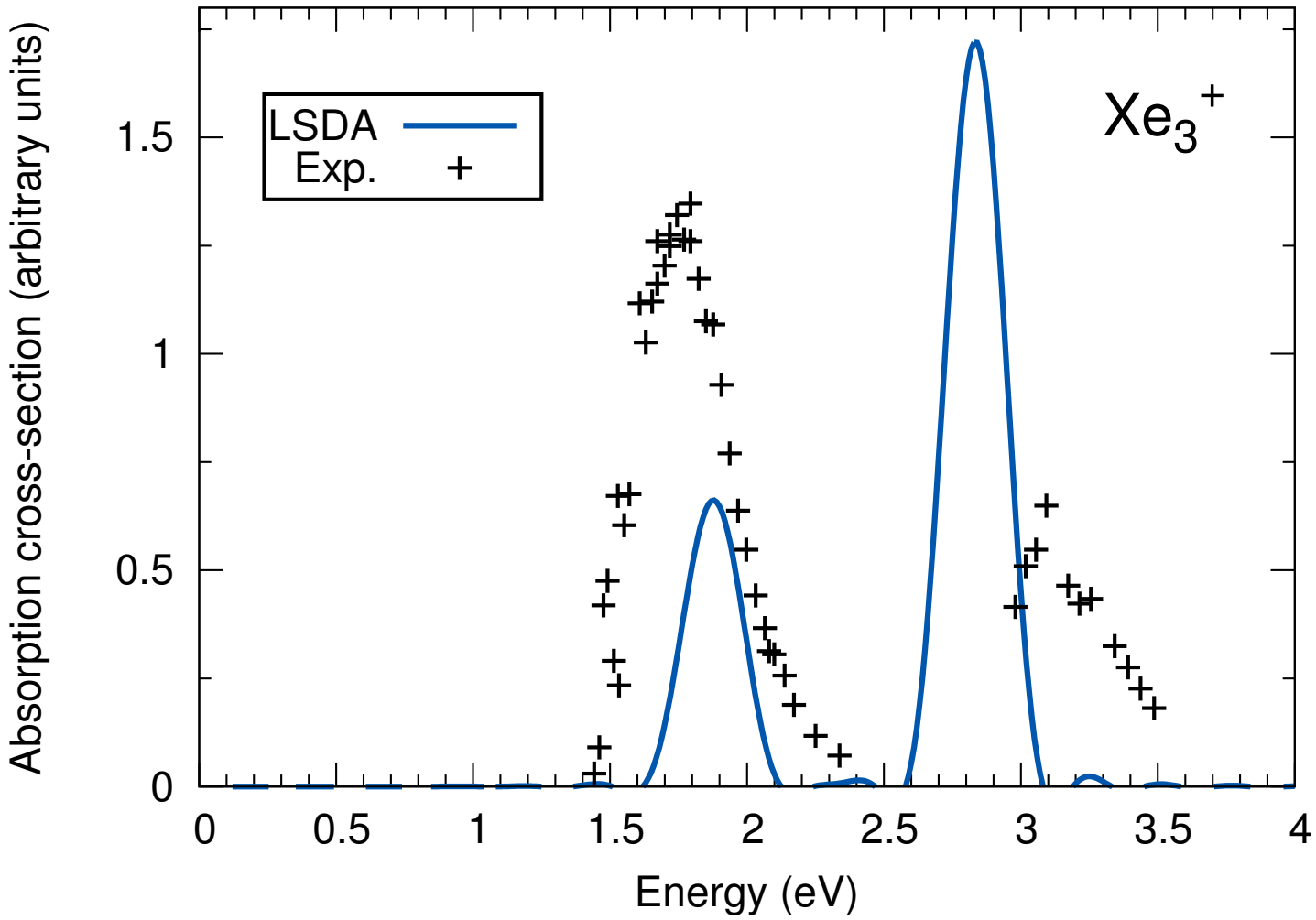
- Neutral rare-gas clusters are van der Waals bound and their first electronic transition is in the UV region.
- Upon the removal of one electron the bonding becomes much stronger and the absorption shifts to the visible region.




Haberland *et al*, PRL **67**, 3290 (1991)

# Something is wrong...



# Bug hunting

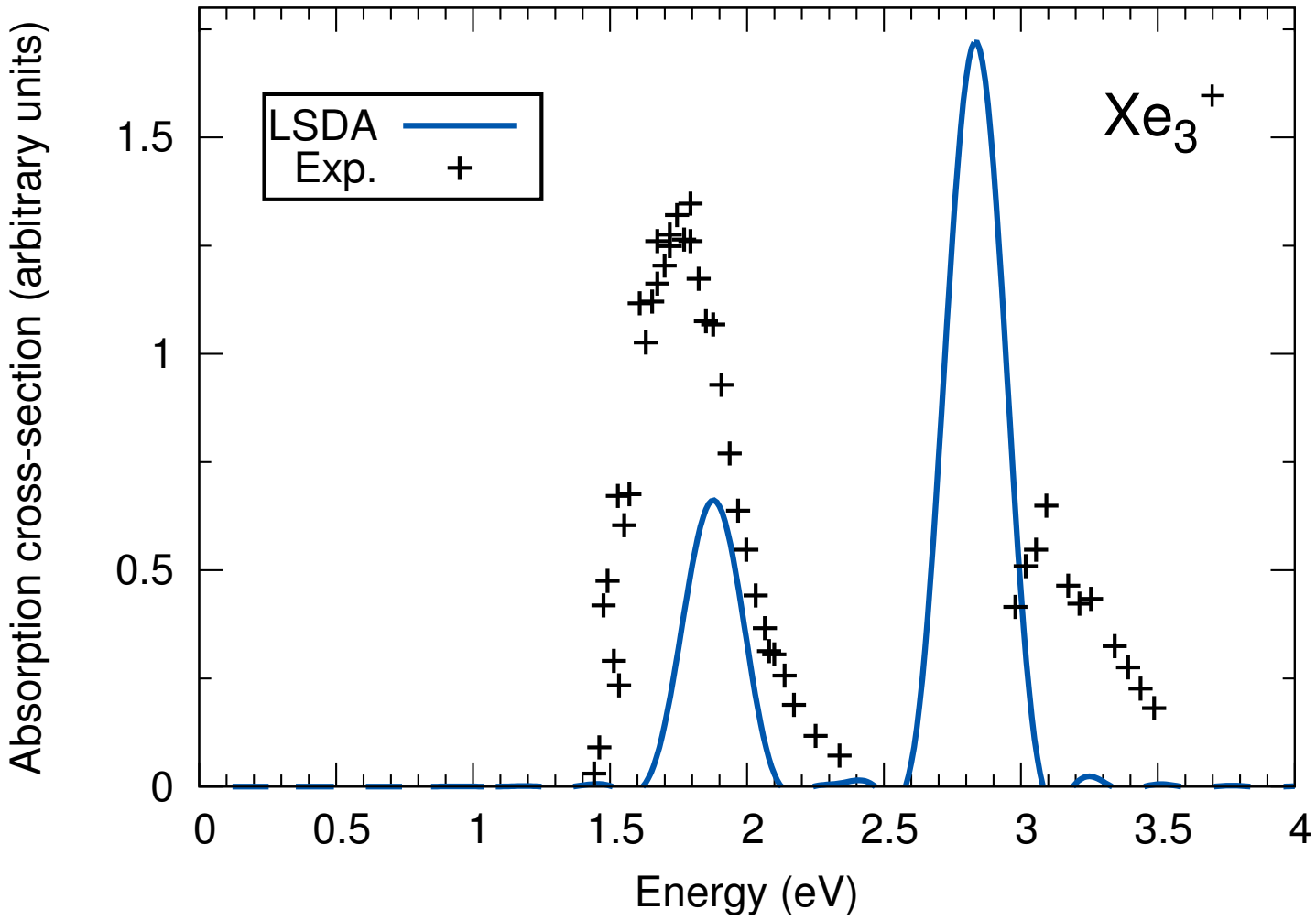
## r792

```
2004-05-19 13:13  micael

  * [r792] src/h_inc.F90:

    *) Bug fixed. There was a sign wrong in the vlpsi routine
    when using spinors.
```

# Bug hunting

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# Are we missing something?

- Geometries.
- Inclusion of relativistic effects through the pseudopotential.
- Exchange and correlation potential.

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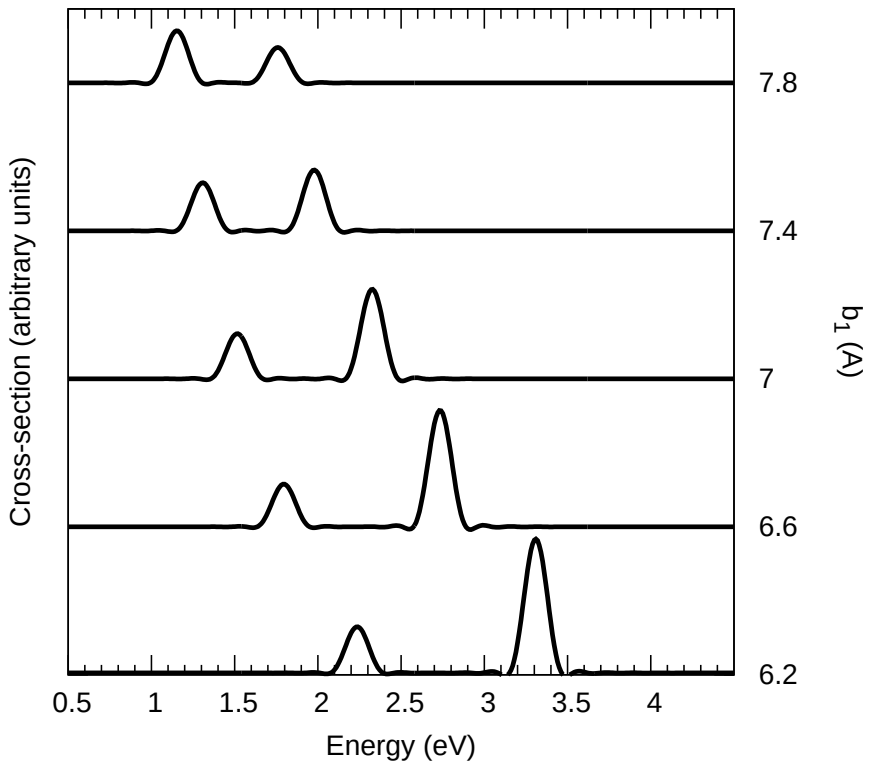
# Geometries




The relative intensities only get inverted at very large bond lengths.

# Relativistic effects: spin-orbit coupling, part II

$$\hat{v}^{\mathrm{KB}} = v_{\mathrm{loc}} + \sum_{l,m} \frac{|\psi_{l,m}\delta v_l\rangle\langle\psi_{l,m}\delta v_l|}{\langle\psi_{l,m}|\delta v_l|\psi_{l,m}\rangle} \qquad \delta v_l = v_l^{\mathrm{Avg}} - v_{\mathrm{loc}}$$

$$+ \sum_{l,m} \frac{|\psi_{l,m}v_l^{\mathrm{SO}}\rangle\mathbf{L}\cdot\mathbf{S}\langle\psi_{l,m}v_l^{\mathrm{SO}}|}{\langle\psi_{l,m}|v_l^{\mathrm{SO}}|\psi_{l,m}\rangle}$$

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# Relativistic effects: spin-orbit coupling, part II

## r2662

```
2007-01-24 19:05  micael

  * [r2662] liboct/oct_gsl_f.c, src/Makefile.am, src/epot.F90,
    src/epot_inc.F90, src/gs.F90, src/h.F90, src/h_inc.F90,
    src/hgh_projector.F90, src/hgh_projector_inc.F90,
    src/kb_projector.F90, src/kb_projector_inc.F90, src/lcao.F90,
    src/lcao_inc.F90, src/liboct.F90, src/math.F90, src/ps.F90,
    src/ps_upf.F90, src/rkb_projector.F90, src/scf.F90,
    src/specie.F90, src/td_calc.F90, src/unocc.F90:

    *) Changed the way the spin-orbit coupling in computed when using
    norm-conserving pseudo-potentials. Now the Kleinman-Bylander
    projectors are build using the total angular momentum
    eigenfunctions. In order to do this I had to change a bit the
    projectors part in the code.

    This new scheme requires the use of j-dependent pseudo-potentials
    that are only available when using the UPF format.
```

# Relativistic effects: spin-orbit coupling, part II

- Spin-orbit coupling is included using j-dependent pseudopotentials in the fully-separable Kleinman and Bylander form:

$$v^{\mathrm{PP}} = v_{loc} + \sum_{l,j,m_j} \frac{\left|\delta v_{l,j}\ \phi_{l,j,m_j}\right\rangle \left\langle \phi_{l,j,m_j}\ \delta v_{l,j}\right|}{\left\langle \phi_{l,j,m_j}\right|\ \delta v_{l,j}\ \left|\phi_{l,j,m_j}\right\rangle}$$

$$|\phi_{l,j,m_j}\rangle = |R_{l,j}\rangle |\Phi^{l,j}_{m_j}\rangle$$

- $|\Phi^{l,j}_{m_j}\rangle$ are the total angular momentum eigenfunctions:

$$|\Phi^{l,j}_{m_j}\rangle = \begin{cases} \left(\frac{l+m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle|\uparrow\rangle + \left(\frac{l-m}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m+1}\rangle|\downarrow\rangle & \text{if } j = l+\frac{1}{2} \\ \left(\frac{l-m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m-1}\rangle|\uparrow\rangle - \left(\frac{l+m}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle|\downarrow\rangle & \text{if } j = l-\frac{1}{2} \end{cases}$$

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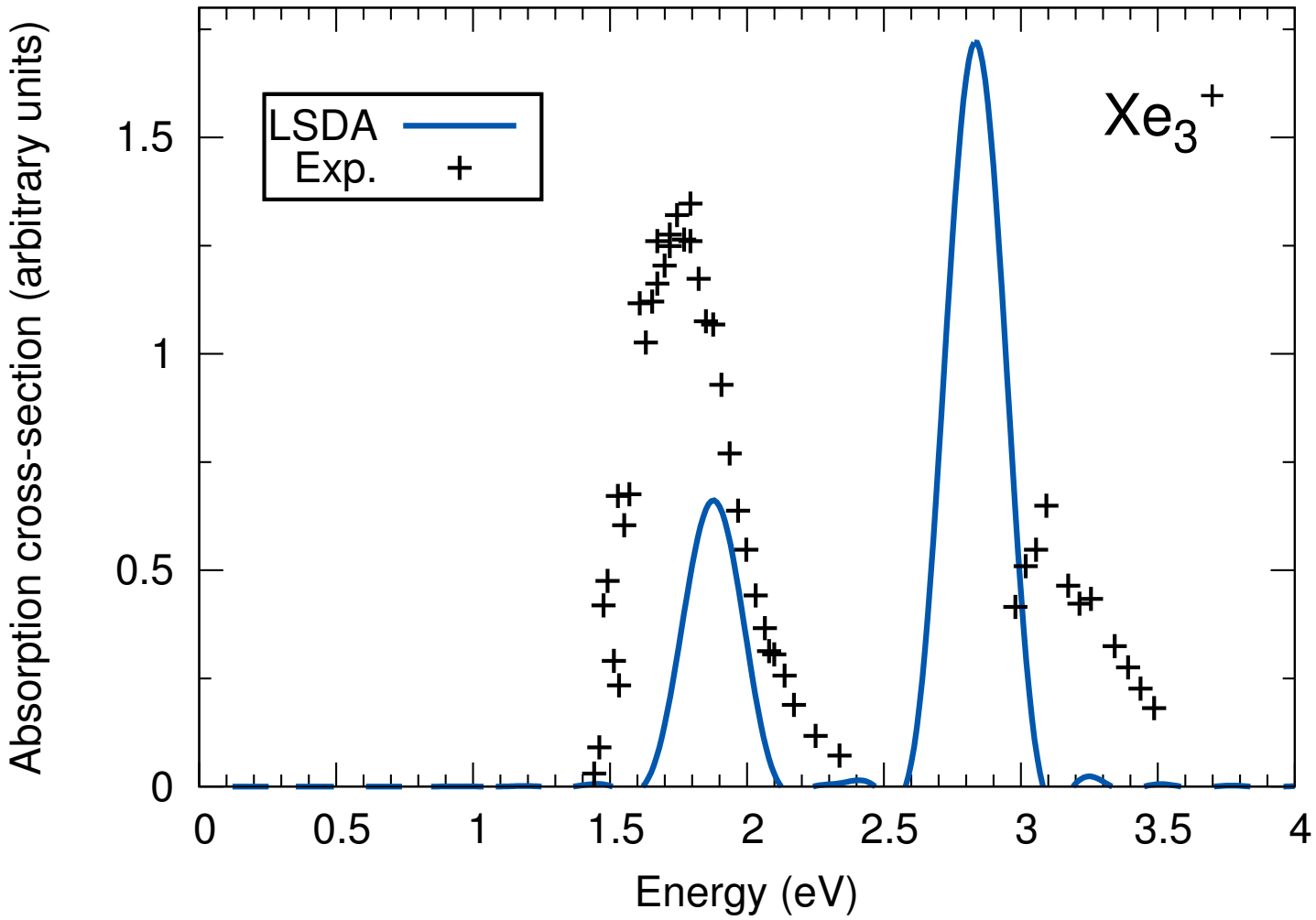
# Relativistic effects: spin-orbit coupling, part II



# Relativistic effects: spin-orbit coupling, part III

## r3988

```
2008-03-31 15:06  fnog

  * [r3988] src/h_sys/epot.F90, src/h_sys/projector.F90,
    src/h_sys/rkb_projector.F90:

    Artificial tuning of the spin-orbit coupling strength via a
    parameter in the input file: SOStrength. Setting this value
    to 0.0 turns off spin-orbit terms in the hamiltonian, and
    setting it to 1.0 corresponds to full spin-orbit. It
    might be useful for someone to play a bit with SO...
```

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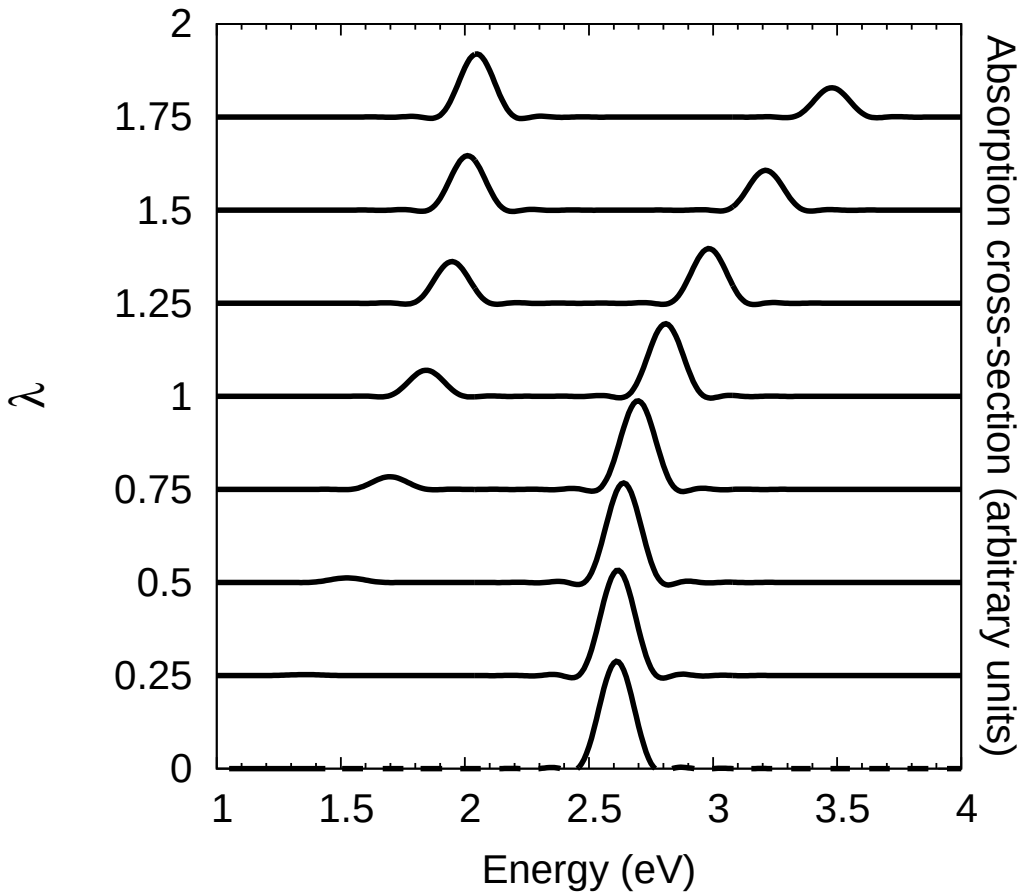
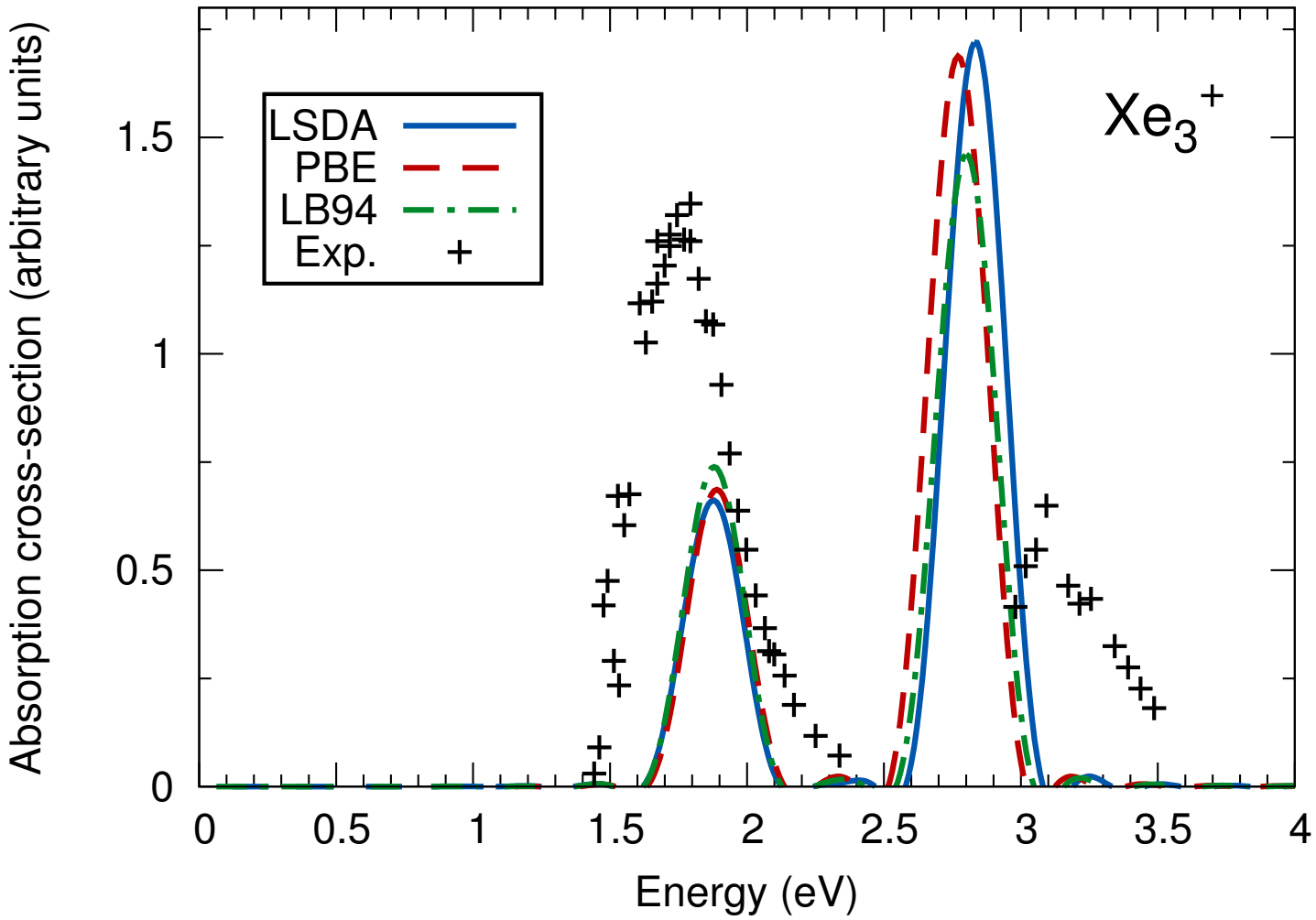
# Relativistic effects: spin-orbit coupling, part III



# Exchange and correlation



# Hartree-Fock

## r3389

```
2007-10-22 09:40  acastro

  * [r3389] src/h_sys/h.F90, src/h_sys/h_inc.F90,
    src/h_sys/v_ks.F90, src/main/run.F90,
    src/states/states.F90:

    Added a Hartree-Fock mode (HartreeFock = yes). It is
    horribly slow as expected. I have put it because optimal
    control theory for many electrons systems involves an
    equation analogous to td Hartree Fock.

    Of course it is a preliminary commit and some things are
    missing, but it seems to give the right eigenvalues for H2
    and benzene.
```

# Hartree-Fock

$$E_{\mathrm{x}} = -\frac{1}{2}\sum_{\sigma}\sum_{i,j}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{r}'\,\frac{\psi^*_{i\sigma}(\boldsymbol{r})\psi^*_{j\sigma}(\boldsymbol{r}')\psi_{i\sigma}(\boldsymbol{r}')\psi_{j\sigma}(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$V^{(i)}_{\mathrm{x}\sigma}(\boldsymbol{r}) = -\frac{1}{\psi^*_{i\sigma}(\boldsymbol{r})\psi_{i\sigma}(\boldsymbol{r})}\sum_{j}\int \mathrm{d}\boldsymbol{r}'\,\frac{\psi^*_{i\sigma}(\boldsymbol{r})\psi^*_{j\sigma}(\boldsymbol{r}')\psi_{i\sigma}(\boldsymbol{r}')\psi_{j\sigma}(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

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# Hybrid functionals

## r3567

```
2007-11-21 12:50  marques

  * [r3567] src/h_sys/h.F90, src/h_sys/h_inc.F90,
    src/h_sys/v_ks.F90, src/scf/scf.F90,
    src/xc/functionals.F90, src/xc/xc.F90:

    Now we can perform also hybrid calculations within
    Hartree-Fock theory. In doing this, I encountered a series
    of questions:
    *) Is the total energy in Hartree-Fock well calculated? I
       believe that there are a couple of terms missing from the
       formula. Alberto?
    *) H_psi is currently a mess. We have 3 or 4 different terms
       to calculate the action of a vector potential, for
       example. This will need some serious cleaning
```

# Hybrid functionals

$$E_{\mathrm{xc}}^{\mathrm{Hybrid}} = \alpha E_{\mathrm{x}}^{\mathrm{HF}} + (1-\alpha) E_{\mathrm{x}}^{\mathrm{GGA}} + E_{\mathrm{c}}^{\mathrm{GGA}}$$

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# Hartree-Fock + noncollinear magnetism

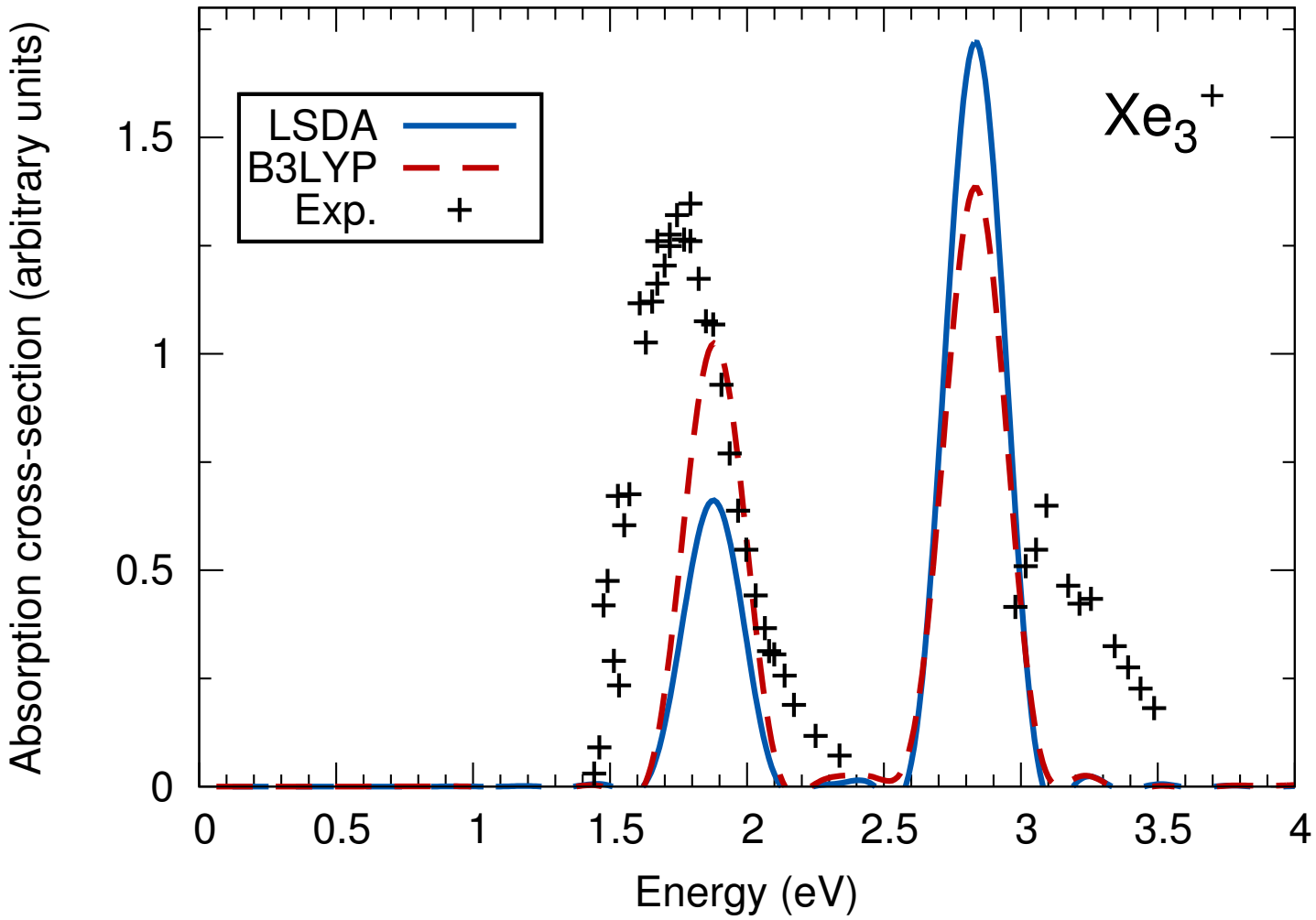
## r5628

```
2009-06-24 14:15  marques

  * [r5628] libxc/src/mgga_x_br97.c, src/Makefile.am, libxc/src/gga.c,
    libxc/src/gga_c_am05.c, libxc/src/gga_c_p86.c, libxc/src/gga_perdew.c,
    libxc/src/gga_xc_lb.c, libxc/src/hyb_gga.c, libxc/src/lda.c,
    libxc/src/libxc_master.F90, libxc/src/mgga.c, libxc/src/mgga_c_tpss.c,
    libxc/src/mgga_x_lta.c, libxc/src/mgga_x_m06l.c,
    libxc/src/mgga_x_tau_hcth.c, libxc/src/mgga_x_tpss.c,
    libxc/src/mgga_xc_vsxc.c, libxc/src/test.c, libxc/src/work_gga_becke.c,
    libxc/src/work_mgga_c.c, libxc/src/work_mgga_x.c, libxc/src/xc.h,
    libxc/src/xc_f.c, libxc/testsuite/xc-consistency.c,
    libxc/testsuite/xc-get_data.c, src/hamiltonian/hamiltonian_inc.F90,
    src/species/atomic.F90, src/sternheimer/em_resp_calc_inc.F90,
    src/system/xc_KLI_inc.F90, src/system/xc_OEP_SIC_inc.F90,
    src/system/xc_OEP_inc.F90, src/xc/vxc.F90

    *) Hartree-Fock now works with spinors (I hope)
    *) Added Becke-Roussel Meta-GGA. This one should be working as it was
       tested against a piny_md.
    *) Because of that i had to change slightly the interface to libxc
```

# B3LYP: going in the right direction



# Exact-exchange with noncollinear magnetism

## r????

```
To be commited...
```

Work done by Pedro Melo and Myrta Grüning

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# Exact-exchange with noncollinear magnetism

OEP equations in noncollinear spin DFT:

$$\int d^3r' \left\{ v_x(\boldsymbol{r}')\chi_{nn}(\boldsymbol{r}',\boldsymbol{r}) - \boldsymbol{B}_x(\boldsymbol{r}')\cdot\boldsymbol{\chi}_{mn}(\boldsymbol{r}',\boldsymbol{r}) \right\} =$$

$$= -\int d^3r' \sum_k \left\{ \phi_k^\dagger(\boldsymbol{r}) G_k(\boldsymbol{r},\boldsymbol{r}') \frac{\delta E_x}{\delta \phi_k^\dagger(\boldsymbol{r}')} + c.c. \right\}$$

$$\int d^3r' \left\{ v_x(\boldsymbol{r}')\boldsymbol{\chi}^{(i)}_{nm}(\boldsymbol{r}',\boldsymbol{r}) - \sum_{j=1}^{3} \boldsymbol{B}_x^{(j)}(\boldsymbol{r}')\chi^{(j,i)}_{mm}(\boldsymbol{r}',\boldsymbol{r}) \right\} =$$

$$= -\mu_B \int d^3r' \sum_k \left\{ \phi_k^\dagger(\boldsymbol{r})\boldsymbol{\sigma}_i G_k(\boldsymbol{r},\boldsymbol{r}') \frac{\delta E_x}{\delta \phi_k^\dagger(\boldsymbol{r}')} + c.c. \right\} \quad i = 1,2,3$$

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# Exact-exchange with noncollinear magnetism

KLI approximation in noncollinear spin DFT:

$$M^{\mu\nu}(\boldsymbol{r}) v_{x,\nu}(\boldsymbol{r}) = \Lambda_x^{\mu}(\boldsymbol{r})$$

$$M^{\mu\nu}(\boldsymbol{r}) = \begin{pmatrix} n(\boldsymbol{r}) & -\frac{m_x(\boldsymbol{r})}{\mu_B} & -\frac{m_y(\boldsymbol{r})}{\mu_B} & -\frac{m_z(\boldsymbol{r})}{\mu_B} \\ -\frac{m_x(\boldsymbol{r})}{\mu_B} & n(\boldsymbol{r}) & 0 & 0 \\ -\frac{m_y(\boldsymbol{r})}{\mu_B} & 0 & n(\boldsymbol{r}) & 0 \\ -\frac{m_z(\boldsymbol{r})}{\mu_B} & 0 & 0 & n(\boldsymbol{r}) \end{pmatrix}$$

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# Exact-exchange with noncollinear magnetism

KLI approximation in noncollinear spin DFT:

$$M^{\mu\nu}(\boldsymbol{r})v_{x,\nu}(\boldsymbol{r}) = \Lambda_x^{\mu}(\boldsymbol{r})$$

$$\Lambda_x(\boldsymbol{r}) = \Lambda_x^{\text{Slater}}(\boldsymbol{r}) + \Lambda_x^{\text{Resp}}(\boldsymbol{r})$$

$$\Lambda_{x,i}^{\text{Slater}}(\boldsymbol{r}) = \frac{1}{2}\sum_{k=1}^{N}\left[\phi_k^{\dagger}(\boldsymbol{r})\sigma^i\frac{\delta E_x}{\delta\phi_k(\boldsymbol{r})} + c.c.\right]$$

$$\Lambda_{x,i}^{\text{Resp}}(\boldsymbol{r}) = \frac{1}{2}\sum_{k=1}^{N}\left[\phi_k^{\dagger}(\boldsymbol{r})\sigma^i\phi_k(\boldsymbol{r})\Delta v_k^{KLI} + c.c.\right]$$

$$\Delta v_k^{KLI} = \int d^3r\left\{\theta_k\phi_k^{\dagger}(\boldsymbol{r})\left[v_x(\boldsymbol{r}) + \mu_B\boldsymbol{\sigma}\cdot\boldsymbol{B}_x(\boldsymbol{r}) - u_{x,k}^{\dagger}(\boldsymbol{r})\right]\phi_k(\boldsymbol{r}) + c.c.\right\}$$

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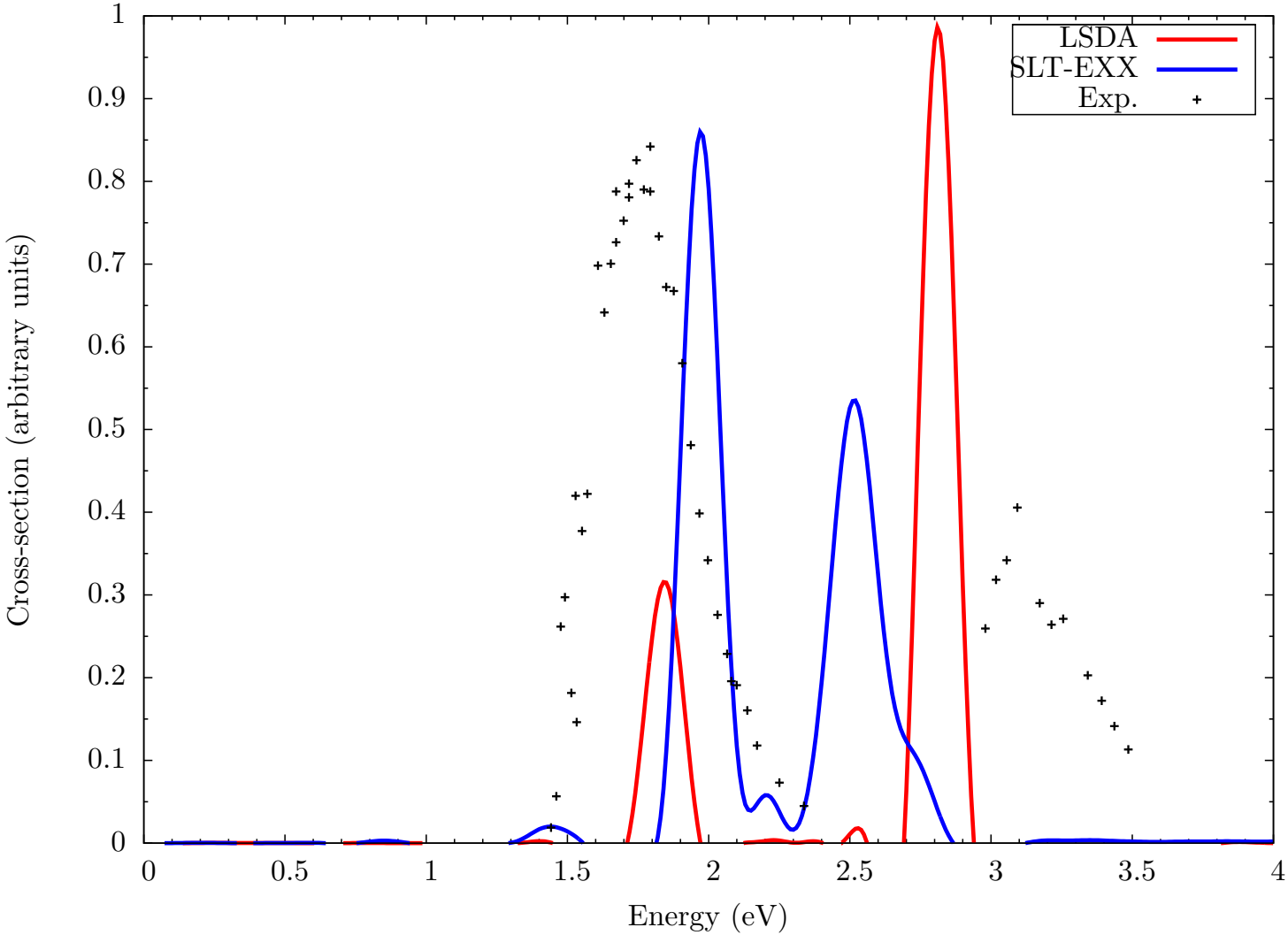
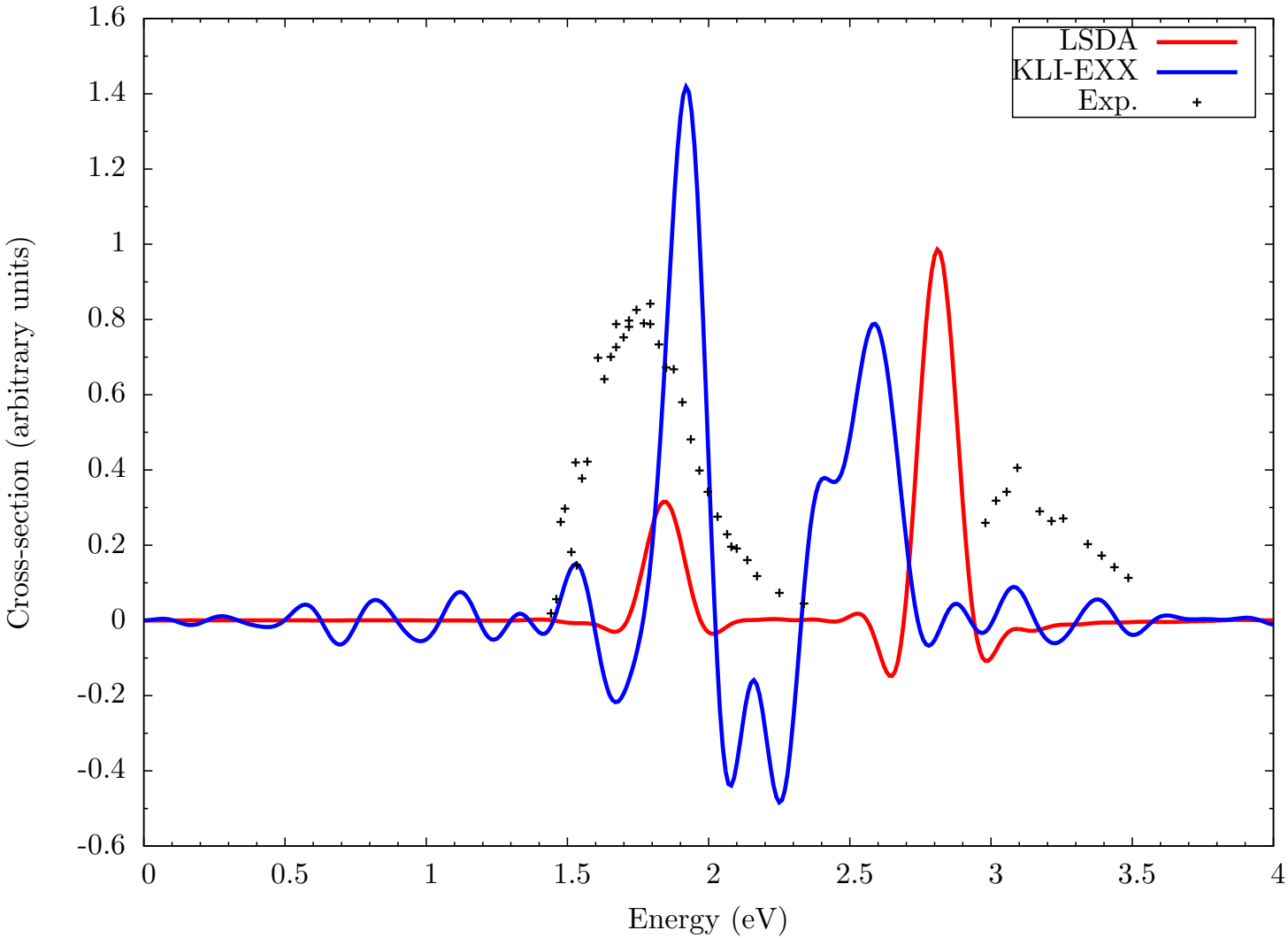
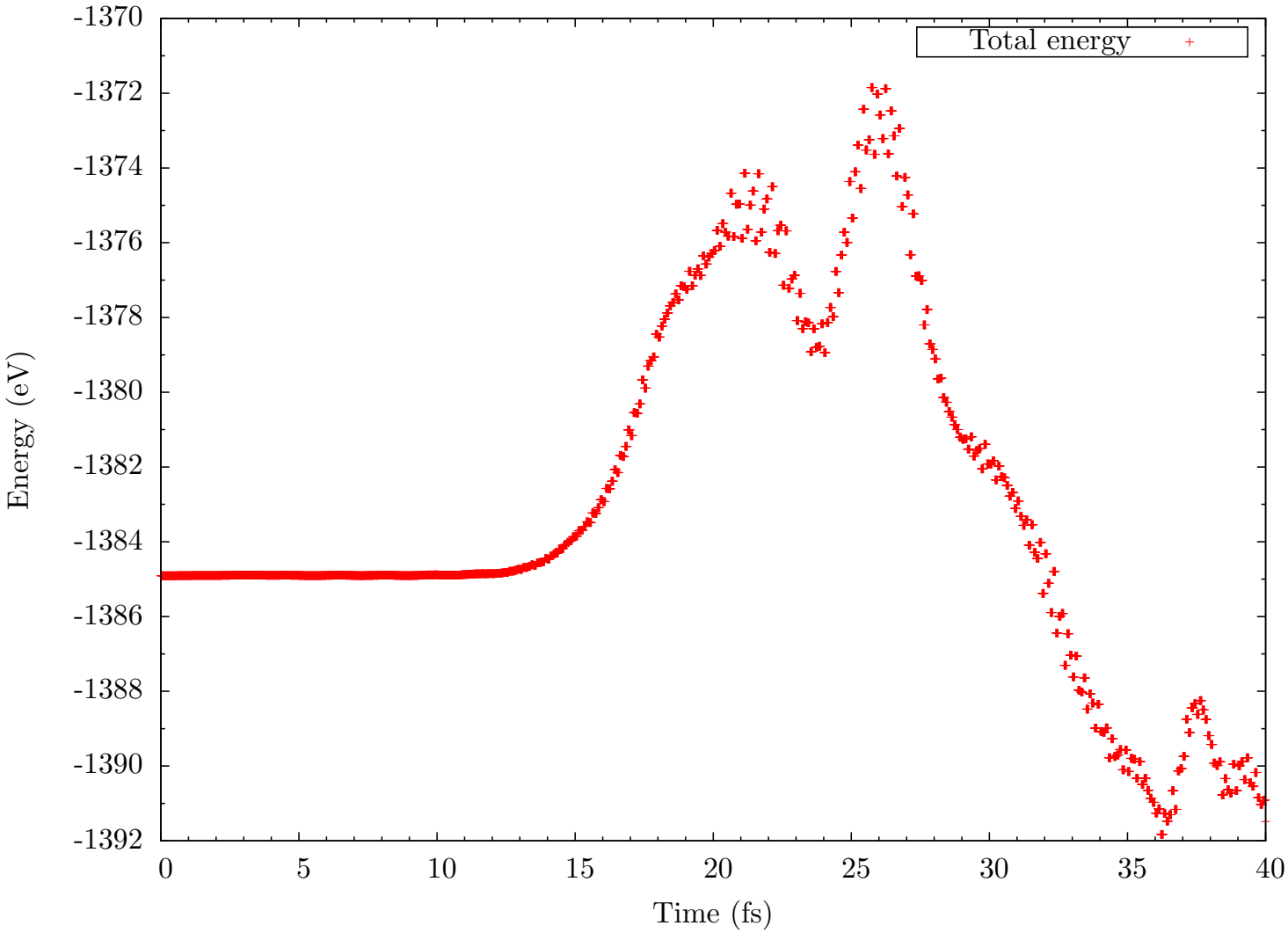
# Slater potential: much better!



# KLI: not so good



# KLI: not so good

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# The never ending story

Future work:

- Check again KLI
- Self-interaction correction with noncollinear magnetism
- Cationic argon clusters

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# Conclusions

- What is useless to you might be useful to someone else.
- Playing with the animal is good (but don't damage it, please).
- There is a correlation between the amount of alcohol consumed and the productivity of the developers.
- The urge to solve mysteries is a driving force for the development of Octopus.

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