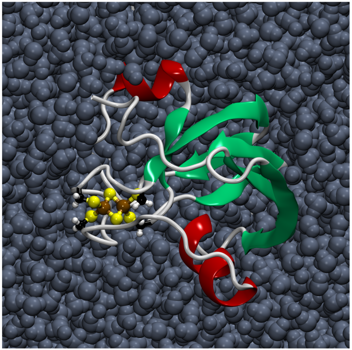
Magnetic Exchange & Magnetostructural Dynamics in Ferredoxins

Nisanth N. Nair

Indian Institute of Technology Kanpur
Kanpur 208016, India
http://home.iitk.ac.in/~nnair

Dec. 18, 2009, Bangalore

Motivation



- Iron–sulfur proteins: electron transport in biology
- Ferredoxin: paramagnetic Fe centers bridged by S
- [2Fe–2S] type: Fe sites interact by "superexchange"; antiferromagnetic alignment of electrons

$\mathrm{Fe_A}$ (S_A=5/2) - - - - $\mathrm{Fe_B}$ (S_B=5/2)

Beinert et al. (1997) *Science* 277:653

Magnetic Coupling

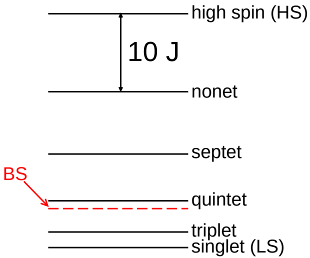
- Magnetic exchange interactions
  - result to a low–spin ground state ⇒ antiferromagnetic coupling
  - result to a high–spin ground state ⇒ ferromagnetic coupling
- Magnetic coupling modeled using Heisenberg-Dirac-Van Vleck spin Hamiltonian

$$\hat{H} = -2J\,\hat{\mathsf{S}}_{\mathsf{A}} \cdot \hat{\mathsf{S}}_{\mathsf{B}}$$

- Spin ladder:

$$E^{S} - E^{S-1} = -2JS$$

- Low spin ground state: multireference character



- Poor man's description: single singlet determinant (broken symmetry) $Fe_A(\uparrow\uparrow\uparrow\uparrow\uparrow) \cdots Fe_B(\downarrow\downarrow\downarrow\downarrow\downarrow)$
- Broken symmetry wavefunction is not the true ground state wavefunction
- **How to access structure and dynamics at low–spin state?**

Acknowledgments

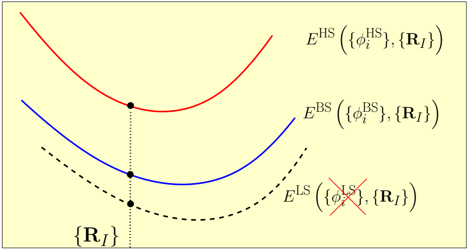
- Dr. Eduard Schreiner (Beckman Institute, USA)
- Prof. Dr. Dominik Marx (RUB, Germany)

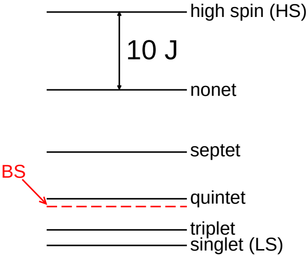
- Dr. Rodolphe Pollet (CEA, France)

- Prof. Dr. Volker Staemmler (RUB, Germay)
- Dr. J. Ribas–Arino (RUB, Germany)

- E. Schreiner, N. N. Nair, R. Pollet, V. Staemmler, and D. Marx (2007) **Proc. Natl. Acad. Sci. USA**, 104:20725–20730
- N. N. Nair, E. Schreiner, R. Pollet, V. Staemmler, and D. Marx (2008) **J. Chem. Theory Comput.**, 4:1174–1188

The Essence





- Estimate E^{HS} ($S = S_{max}$) and E^{BS} ($S = S_{min}$)
- Compute J and thus spin ladder; For e.g.,

$$J = \frac{E^{BS} - E^{HS}}{S_{max}^2}$$

- Estimate E^{LS} from spin ladder (projection)
- Calculate $\mathbf{F}_I^{LS}$ by similar projection $\rightarrow$ dynamics

General Expression for J

$$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S^2_{\max} - S^2_{\min} - \Theta^{\mathrm{BS}} + \Theta^{\mathrm{HS}}}$$

with

$$\Theta = N^{\beta}_{\mathrm{nmag}} - \sum_i^N \sum_j^N f_i^{\alpha} f_j^{\beta} \langle \phi_i^{\alpha} | \phi_j^{\beta} \rangle^2$$

for unrestricted Hartree–Fock theory
(overlap of magnetic orbitals and spin contamination)

Nair et al. (2008) **J. Chem. Theory Comput.**, 4:1174–1188

General Expression for J

$$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S_{\mathrm{max}}^2 - S_{\mathrm{min}}^2 - \Theta^{\mathrm{BS}} + \Theta^{\mathrm{HS}}}$$

- **Weak overlap limit:**
  $\Theta^{\mathrm{BS/HS}} = 0$ and $N^\alpha = N^\beta \rightarrow$ Noodleman formula

  $$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S_{\mathrm{max}}^2}$$

  Noodleman L (1981) *J. Chem. Phys.* 74:5737
- **Strong overlap limit:**
  $\Theta^{\mathrm{HS}} = 0$, $\Theta^{\mathrm{BS}} = N_{\mathrm{mag}}$ and $N^\alpha = N^\beta \rightarrow$ Ruiz formula

  $$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S_{\mathrm{max}}(S_{\mathrm{max}} + 1)}$$

  Ruiz et al. (1999) *J. Comp. Chem.* 20:1391

General Expression for Ground State Energy

$$E^{\text{LS}} = E^{\text{BS}} + J(S_{\text{max}} - S_{\text{min}} + \Theta^{\text{BS}})$$

$$\text{or} \quad E^{\text{LS}} = (1 + c)\, E^{\text{BS}} - c\, E^{\text{HS}}$$

$$\text{where} \quad c = \frac{S_{\text{max}} - S_{\text{min}} + \Theta^{\text{BS}}}{S^2_{\text{max}} - S^2_{\text{min}} - \Theta^{\text{BS}} + \Theta^{\text{HS}}}$$

- Accessing energy of the low–spin state *without* having the low–spin density
- Requirement: Heisenberg Hamiltonian must hold

The Extended Broken Symmetry Approach

- Low spin energy

$$E^{\mathrm{LS}} = (1+c)E^{\mathrm{BS}} - cE^{\mathrm{HS}} \quad = \mathcal{P}E^{\mathrm{BS,HS}}$$

Low spin forces

$$\mathbf{F}_I^{\mathrm{LS}} = (1+c)\mathbf{F}_I^{\mathrm{BS}} - c\mathbf{F}_I^{\mathrm{HS}}$$
$$= -\nabla_{\mathbf{R}_I}\left[(1+c)E^{\mathrm{BS}}\right] + \nabla_{\mathbf{R}_I}\left[cE^{\mathrm{HS}}\right]$$

- Equations of motion

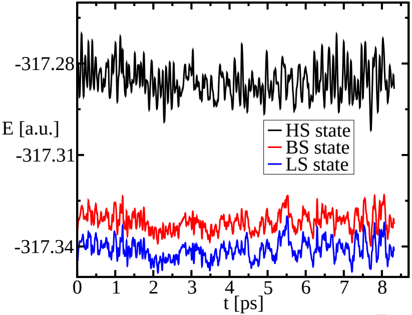
$$M_I\ddot{\mathbf{R}}_I = -\nabla_I\mathcal{P}E^{\mathrm{BS,HS}}$$

$\Rightarrow$ MD, geometry opt. and vibrational anal.

The Extended Broken Symmetry Approach

Car–Parrinello Lagrangian for EBS

$$\mathcal{L}_{\mathrm{CP}}^{\mathrm{LS}} = \frac{1}{2}\sum_I M_I \dot{\mathbf{R}}_I^2 + \frac{1}{2}\sum_i \mu \mathcal{P} \left\langle \dot{\psi}_i | \dot{\psi}_i \right\rangle^{\mathrm{BS,HS}} - \mathcal{P} E^{\mathrm{BS,HS}} + \sum_{i,j} \mathcal{P} \Lambda_{ij}^{\mathrm{BS,HS}} \left(\left\langle \psi_i^{\mathrm{BS,HS}} | \psi_j^{\mathrm{BS,HS}} \right\rangle - \delta_{ij} \right)$$



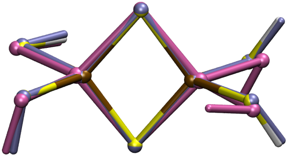
The Extended Broken Symmetry Approach

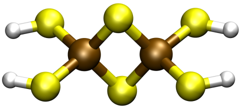
Low spin QM/MM electrostatics

$$E^{\mathrm{LS}}_{\mathrm{QM-MM}} = \mathcal{P}E^{\mathrm{BS,HS}}_{\mathrm{SR}} + \mathcal{P}E^{\mathrm{BS,HS}}_{\mathrm{LR}}$$

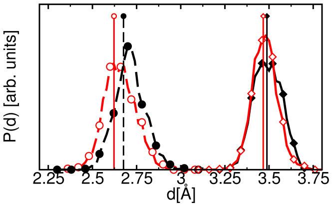
Broken Symmetry vs. Extended Broken Symmetry

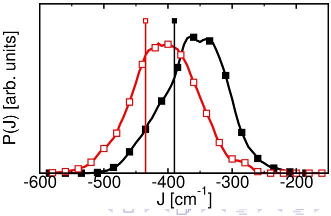
- Minimum energy structure $[Fe_2S_2(SH)_4]^{2-}$ (XC=PBE/PP=USPP/PW=30 Ry)





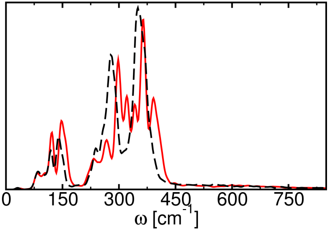
- Distribution function of structural parameters and J (EBS vs. BS)





Broken Symmetry vs. Extended Broken Symmetry (2)

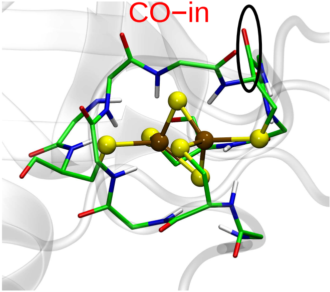
- Vibrational frequencies (EBS vs. BS)

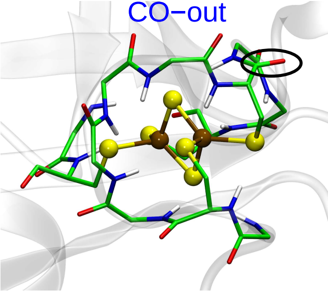


- EBS and BS differ in their structure and dynamics

Anabaena Ferredoxin

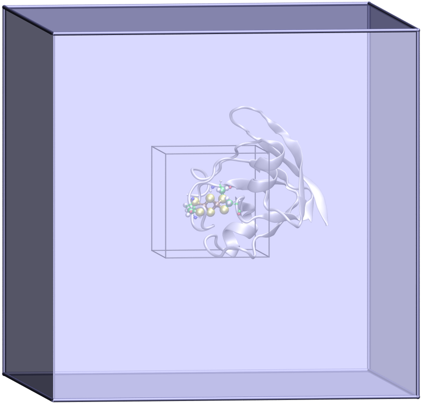
- Redox–induced conformational changes in protein





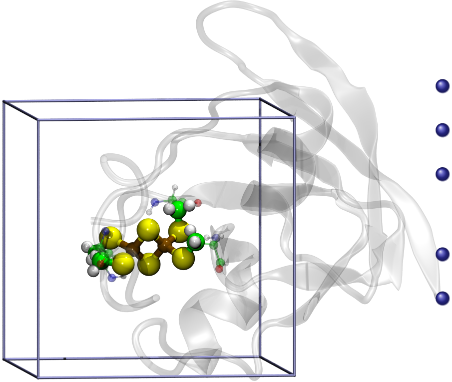
- EBS–QM/MM: CPMD–GROMOS/USPP/Amber FF/16 ps production

Anabaena Ferredoxin: Modeling Aspects (1)



- *Anabaena* Fd (pdb: 1qt9) in CO-in and CO-out form
- 13265 H_2O molecules 23 Na^+ and 5 Cl^- ions
- NVT
- 74 Å cubic box, 300 K
- AMBER94 Force Field
- CPMD/GROMOS interface

Anabaena Ferredoxin: Modeling Aspects (2)

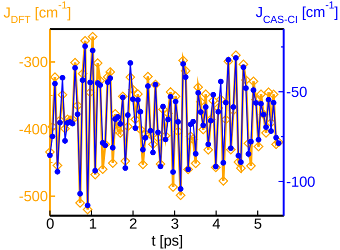


- Spin–polarized DFT
- PBE functional
- Vanderbilt USPP, 30 Ry cutoff
- 21 Å cubic QM box
- EBS–CPMD

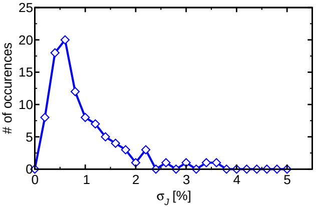
- QM subsystem:
  $[(\cdot - \mathbf{CH_2} - \mathbf{S})_2 - [\mathbf{2Fe} - \mathbf{2S}] - (\mathbf{S} - \mathbf{CH_2})_2 - \cdot]^{2-}$

Validity of the EBS

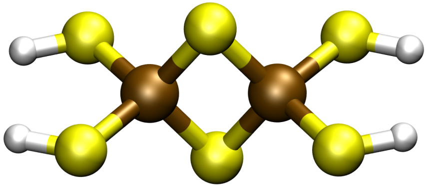
Same dynamics of J within EBS-DFT and CAS-CI

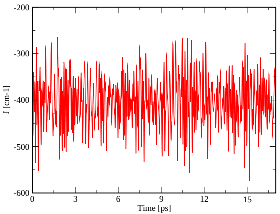


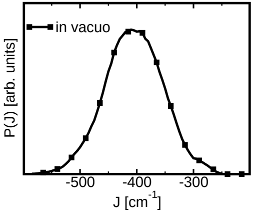
Heisenberg model holds well in asymmetric protein environments.



Effect of Temperature and Environment on J



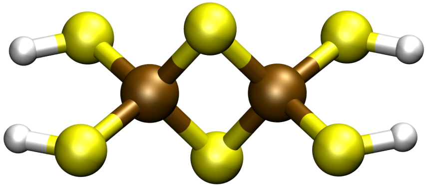


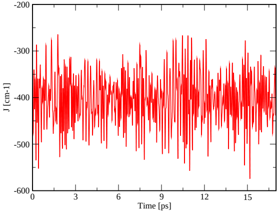


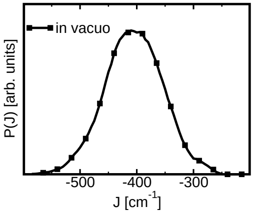
$$G_{\mathbf{PP}}(t) = \frac{\langle \mathbf{P}(t_0) \cdot \mathbf{P}(t_0 + t) \rangle_{t_0}}{\langle \mathbf{P}(t_0) \cdot \mathbf{P}(t_0) \rangle_{t_0}},$$

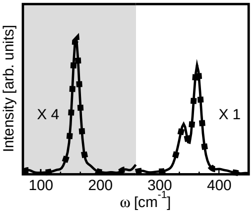
$$G_{\mathbf{PP}}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_{\mathbf{PP}}(t) \exp\left(-i\omega t\right) dt$$

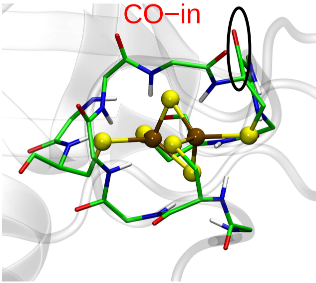
Effect of Temperature and Environment on J

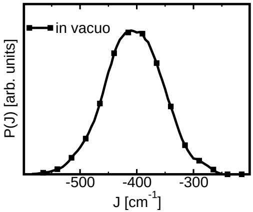


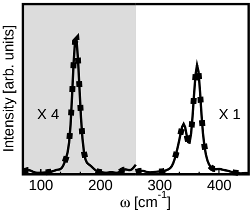


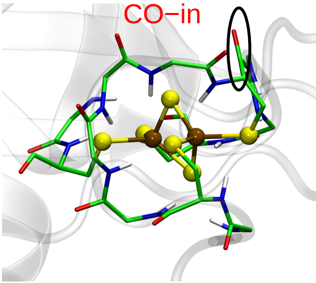


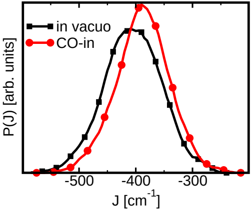



CO–in


in vacuo
P(J) [arb. units]
-500
-400
-300
J [cm^{-1}]


Intensity [arb. units]
X 4
X 1
100
200
300
400
ω [cm^{-1}]


CO–in


in vacuo
CO-in
P(J) [arb. units]
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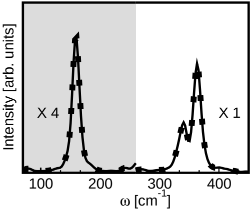
J [cm^{-1}]


X 4
X 1
Intensity [arb. units]
100
200
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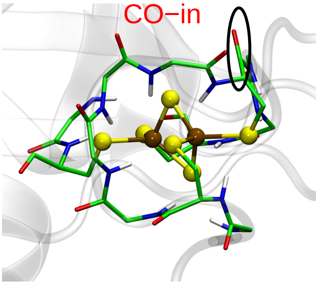
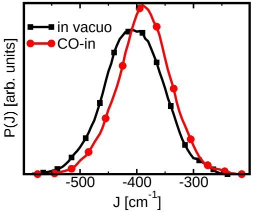
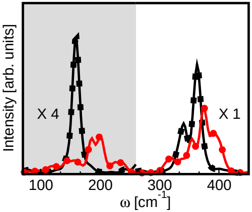
400
ω [cm^{-1}]

Effect of Temperature and Environment on J







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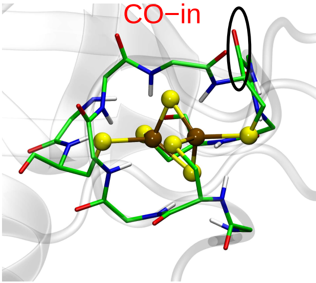

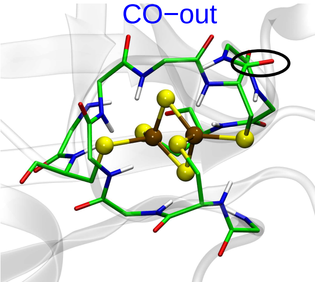

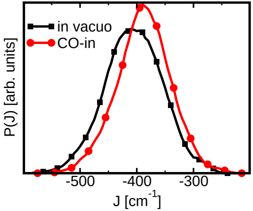

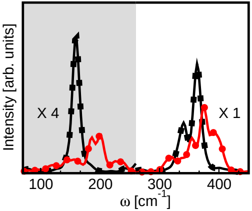

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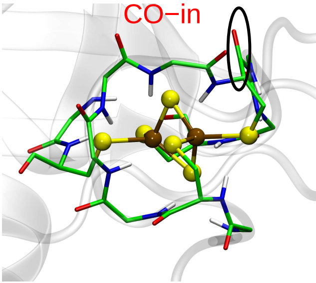

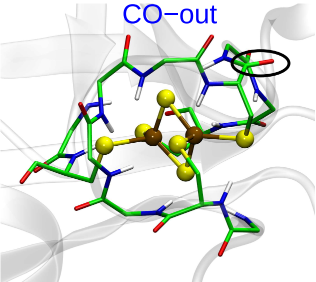

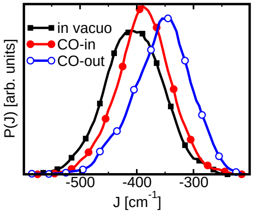

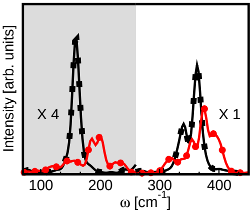

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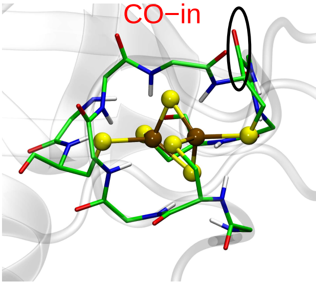
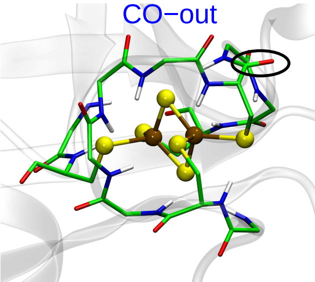
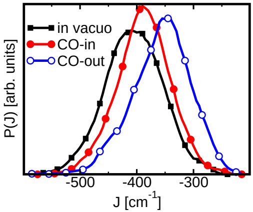
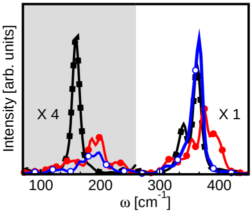
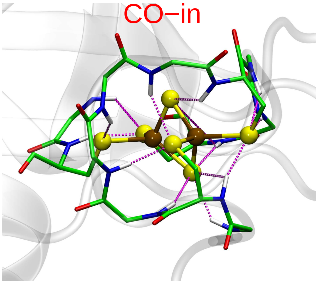
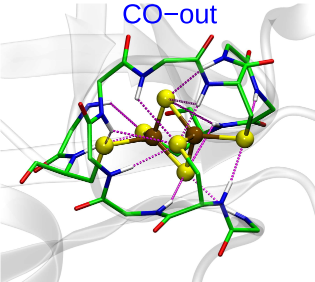


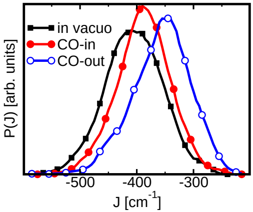


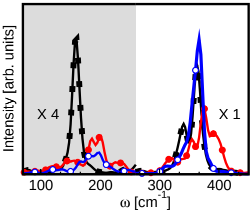




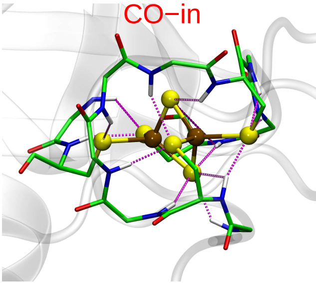

CO−in

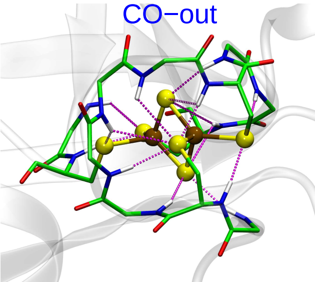

CO−out

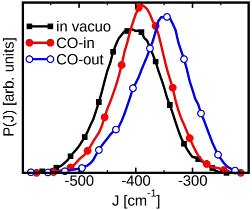

in vacuo
CO-in
CO-out
P(J) [arb. units]
J [cm⁻¹]
-500
-400
-300

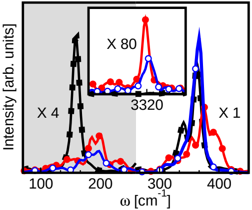

Intensity [arb. units]
ω [cm⁻¹]
X 4
X 1
100
200
300
400

Effect of Temperature and Environment on J



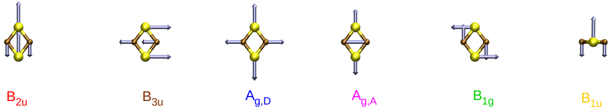






Define a basis set

normal modes $\{\mathbf{q}_\xi\}$ of [2Fe2S] based on D_{2h} symmetry



Dynamical Magnetostructural Analysis

Define a basis set

normal modes $\{\mathbf{q}_\xi\}$ of [2Fe2S] based on $\mathrm{D_{2h}}$ symmetry

Project trajectory of [2Fe2S] on each mode $\{\mathbf{q}_\xi\}$

$$q_\xi(t) = \mathbf{R}_\mathrm{c}(t) \cdot \mathbf{q}_\xi$$

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$G_{\xi,\xi'}(t) \rightarrow G_{\xi,\xi'}(\omega)$; minimize $\int \left|G_{\xi,\xi'}(\omega)\right| d\omega$

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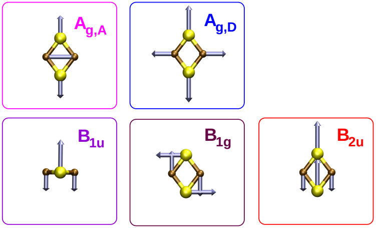
Cross Correlation $G_{\xi,J}(\omega)$ with the new basis set

$G_{\xi,J}(t) \rightarrow G_{\xi,J}(\omega)$

Dynamical Magnetostructural Analysis: Results



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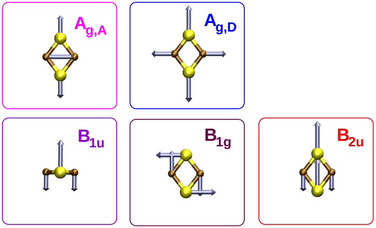

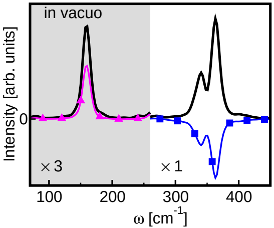

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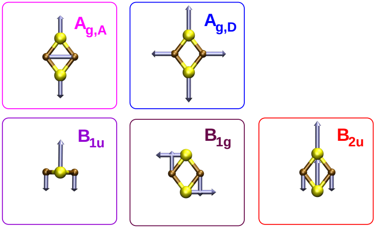

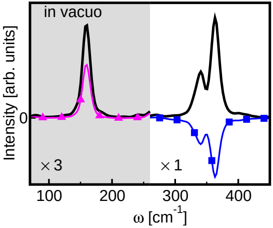

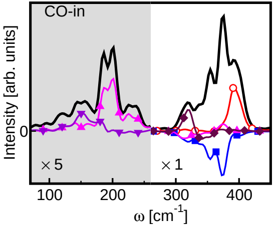

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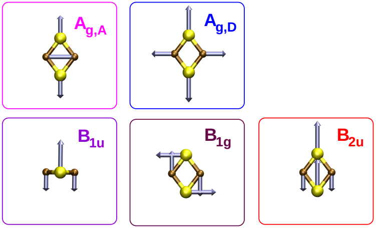
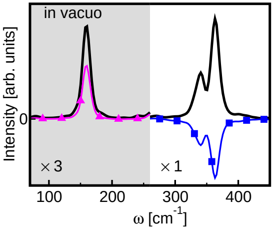
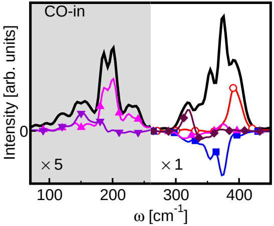
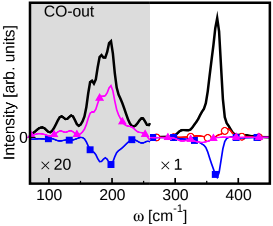
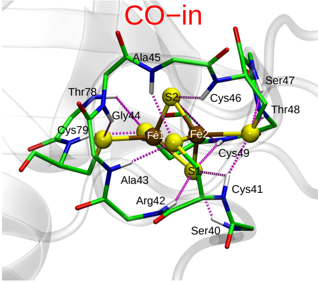


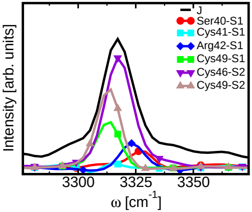






The Role of Hydrogen Bonds





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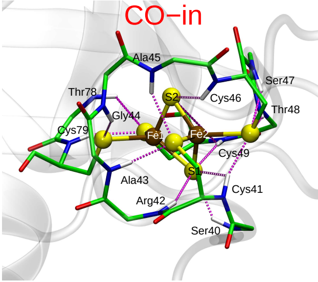
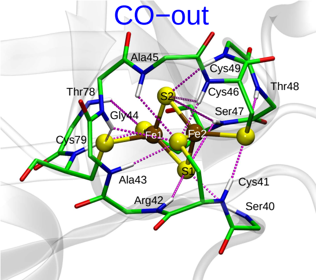
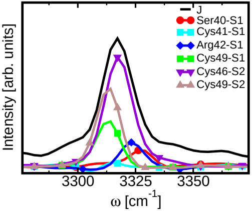
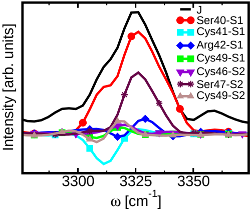
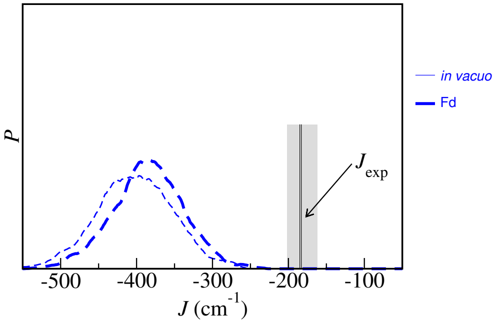




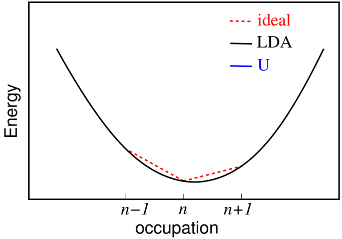




Why J is overestimated?



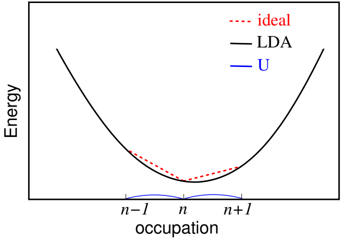
Hubbard U correction; Linear Response approach



- Self interaction stabilizes fractional occupation

- Delocalization of electrons to ligands $\Rightarrow$ stronger bond
- Increases the value of J
- Solution: Minimize delocalization

Hubbard U correction; Linear Response approach



- Self interaction stabilizes fractional occupation

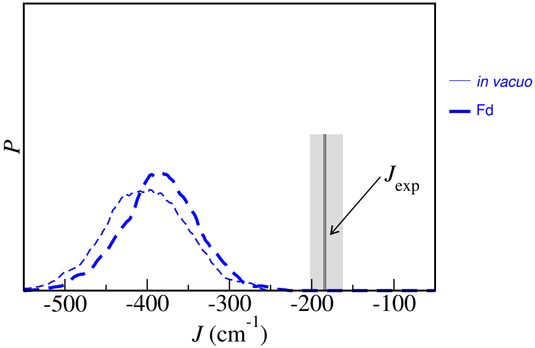
Cococcioni & de Gironcoli PRB 2005
Marzari et al. PRL 2006

- Hubbard correction to retain linearity

$$E_U = \frac{1}{2}\sum_{I,\sigma} U \ \mathrm{Tr}\left[\mathbf{n}^{I,\sigma}\left(\mathbf{1} - \mathbf{n}^{I,\sigma}\right)\right]$$

- U is curvature of energy–occupation curve $\rightarrow$ from linear response
- $V^{\mathrm{GGA}}(\mathbf{r}) + V^{\mathrm{U}}(\mathbf{r}) \longrightarrow$ new density $\Rightarrow$ a self–consistent procedure

- QM–MM/EBS+U implementation in CPMD (+USPPs) $\rightarrow$ +6% CPU time overhead



N. N. Nair, J. Ribas–Arino, V. Staemmler, and D. Marx, *submitted*

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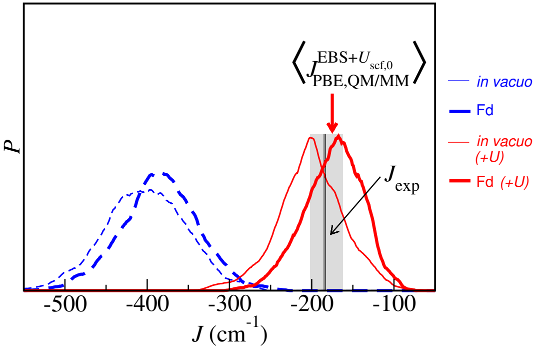

N. N. Nair, J. Ribas–Arino, V. Staemmler, and D. Marx, *submitted*

EBS+U Car–Parrinello Simulations (2)

	Fd (EBS)	Fd (EBS+U)	Xray–Fd
r(Fe1–Fe2)	2.62	2.74	2.75
r(Fe–S)	2.22	2.27	2.29
θ(Fe–S–Fe)	72.2	74.0	75.1

Parameterization of J

- Force–field for complex [2Fe–2S] prosthetic group is now possible
- BUT...J in classical force–fields?? $\Rightarrow$ parameterization of J

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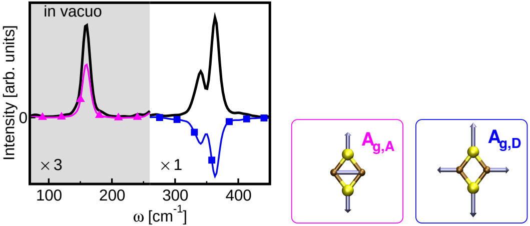
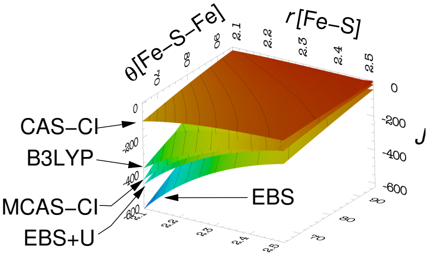
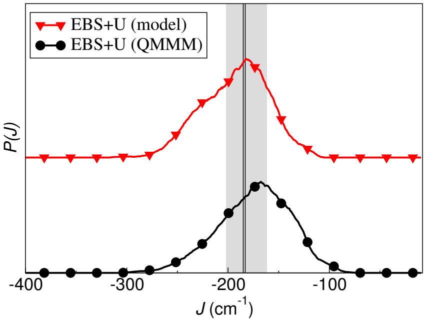


Parameterization of J (2)



$$
\begin{aligned}
J(r,\theta) \quad = \quad & A \exp\left[-\alpha\left(r - r_0\right)\right] + \\
& B \exp\left[-\beta\left(r - r_0\right)\right] \cos\theta + \\
& C \exp\left[-\gamma\left(r - r_0\right)\right] \cos 2\theta
\end{aligned}
$$

Parameterization of J (3)



S. A. Fiethen, V. Staemmler, N. N. Nair, J. Ribas–Arino, E. Schreiner and D. Marx, *submitted*

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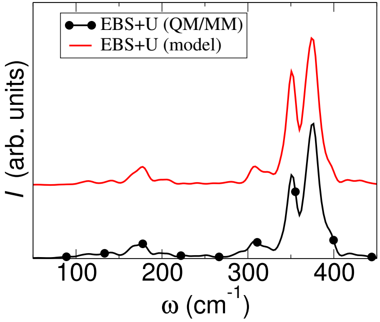

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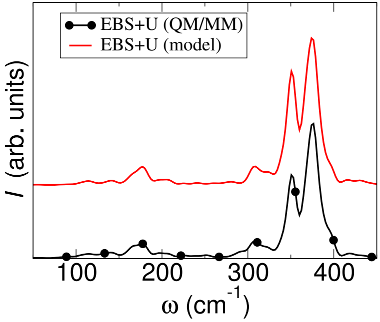


- Parameterization of J reproduces $P(J)$ and $J(\omega)$

S. A. Fiethen, V. Staemmler, N. N. Nair, J. Ribas–Arino, E. Schreiner and D. Marx, *submitted*

Summary

- Dynamics at the low–spin ground state or "any" spin–state by the extended broken symmetry scheme
- Accurate prediction of J values (using DFT)
- Thermal fluctuations change J
- Dynamical magnetostructural analysis
- Complex influence of the protein environment on $J(\omega)$ can be understood
- Parameterization of [2Fe–2S] core and J for classical MD

Thank You For Your Attention

Outlook

Other Magnetic Systems

1. Rieske proteins
2. Multicenter magnetic clusters/embedded proteins

Generalize the Computational Tool

1. General projectors for GGA+U method

Two particle density matrix

$$\Gamma(\mathbf{x}_1', \mathbf{x}_2' | \mathbf{x}_1, \mathbf{x}_2) = \frac{N(N-1)}{2} \times$$
$$\int \Psi^\star(\mathbf{x}_1', \mathbf{x}_2', \ldots, \mathbf{x}_N) \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) d\mathbf{x}_3 \ldots d\mathbf{x}_N,$$

having $\mathbf{x}_i = (\mathbf{r}_i, \sigma_i)$

Questions/Suggestions to Experimentalists

How to measure $P(J)$?

- inelastic neutron scattering (INS)

How to access magnetostructural correlations?
Idea: excite specific vibrations and measure J simultaneously $\Rightarrow$ combination of

- inelastic neutron scattering + resonance Raman
- inelastic neutron scattering + nuclear inelastic scattering (INS+NIS)
  $\Rightarrow$ only Mößbauer active nuclei

General Expression for Ground State Energy

- Heisenberg-Dirac-Van Vleck spin Hamiltonian

$$\hat{H} = -2J\,\hat{S}_\mathrm{A}\cdot\hat{S}_\mathrm{B} = -J(\hat{S}^2 - \hat{S}_\mathrm{A}^2 - \hat{S}_\mathrm{B}^2)$$

- Energy of a spin state

$$E^\mathrm{S} = -J[\mathrm{S}(S+1) - \mathrm{S}_\mathrm{A}(S_\mathrm{A}+1) - \mathrm{S}_\mathrm{B}(S_\mathrm{B}+1)]$$

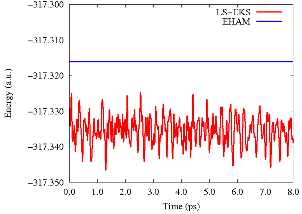
- For practical purpose employing $\langle\hat{S}^2\rangle$

$$\begin{aligned} E^\mathrm{S} &= -J[\langle\hat{S}^2\rangle - S_\mathrm{A}(S_\mathrm{A}+1) - S_\mathrm{B}(S_\mathrm{B}+1)] \\ J &= \frac{E^\mathrm{BS} - E^\mathrm{HS}}{\langle\hat{S}^2\rangle^\mathrm{HS} - \langle\hat{S}^2\rangle^\mathrm{BS}} \end{aligned}$$

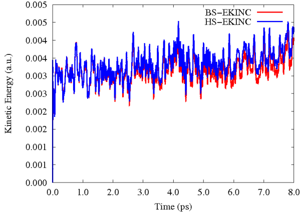
Yamaguchi et al. (1988) *Chem. Phys. Lett.* 149:537

Stability of EBS CP Dynamics

Total energy



Electronic kinetic energy



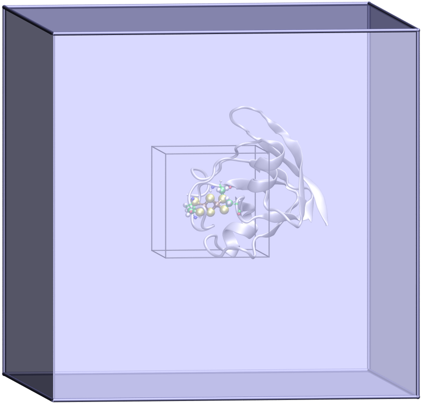
Average Structure Parameters & J in Protein

	$Fe_2S_2(SH)_4^{2-}$ [a]	Fd_{in} [b]	Fd_{out} [b]	Fd_{in} [c]
distance [Å]				
Fe-Fe	2.64	2.62	2.62	2.75
Fe1-S1	2.18	2.22	2.21	2.28
Fe2-S2	2.18	2.17	2.18	2.18
J [cm^{-1}]	-403	-386	-360	–

[a] *in vacuo* ;
[b] solvated protein;
[c] X-ray diffraction data

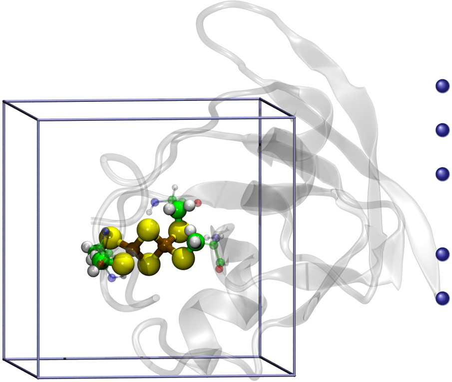
Experimental J for Spinach ferredoxin: -183 cm^{-1}

Modeling Aspects: MM



- *Anabaena* Fd (pdb: 1qt9) in CO-in and CO-out form
- 13265 H_2O molecules 23 Na^+ and 5 Cl^- ions
- NVT
- 74 Å cubic box, 300 K
- AMBER94 Force Field
- CPMD/GROMOS interface

Modeling Aspects: QM



- Spin–polarized DFT
- PBE functional
- Vanderbilt USPP, 30 Ry cutoff
- 21 Å cubic QM box
- EBS–CPMD

- QM subsystem:
  $[(\cdot - \mathbf{CH_2} - \mathbf{S})_2 - [\mathbf{2Fe} - \mathbf{2S}] - (\mathbf{S} - \mathbf{CH_2})_2 - \cdot]^{2-}$

General Expression for J

$$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S^2_{\mathrm{max}} - S^2_{\mathrm{min}} - \Theta^{\mathrm{BS}} + \Theta^{\mathrm{HS}}}$$

with

$$\Theta = N^{\beta}_{\mathrm{nmag}} + 2 \int \Gamma(\mathbf{r}_1\alpha, \mathbf{r}_2\beta | \mathbf{r}_1\beta, \mathbf{r}_2\alpha) \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

Γ is the two particle density matrix

Löwdin P. O. (1955) *Phys. Rev.* 97:1474

Wang et al. (1995) *J. Chem. Phys.* 102:3477

General Expression for J

$$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S^2_{\mathrm{max}} - S^2_{\mathrm{min}} - \Theta^{\mathrm{BS}} + \Theta^{\mathrm{HS}}}$$

with

$$\Theta = N^{\beta}_{\mathrm{nmag}} - \sum_i^N \sum_j^N f_i^{\alpha} f_j^{\beta} \langle \phi_i^{\alpha} | \phi_j^{\beta} \rangle^2$$

for unrestricted Hartree–Fock theory
(overlap of magnetic orbitals and spin contamination)

General Expression for J

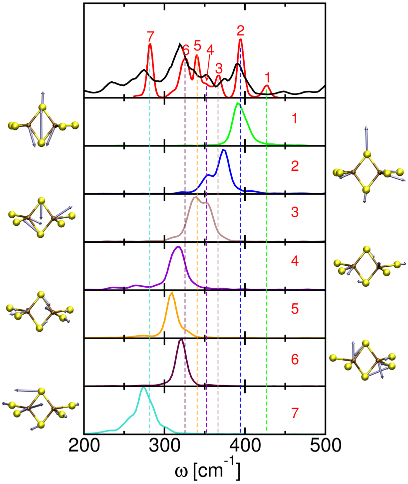
$$J = \frac{E^{\mathrm{BS}} - E^{\mathrm{HS}}}{S^2_{\mathrm{max}} - S^2_{\mathrm{min}} - \Theta^{\mathrm{BS}} + \Theta^{\mathrm{HS}}}$$

For a pure spin state:
$\Theta = 0 \implies \langle \hat{S}^2 \rangle = S(S+1)$

Nair et al. (2008) **J. Chem. Theory Comput.**, 4:1174–1188

Comparison with Experiment

- Modes from principal component analysis on the QM/MM trajectory



Effect of Overlap of Magnetic Orbitals

$$\mathbf{F}_I^{\mathrm{LS}} = (1+c)\mathbf{F}_I^{\mathrm{BS}} - c\mathbf{F}_I^{\mathrm{HS}}$$

$$c = \frac{S_{\mathrm{max}} - S_{\mathrm{min}} + \Theta^{\mathrm{BS}}}{S_{\mathrm{max}}^2 - S_{\mathrm{min}}^2 - \Theta^{\mathrm{BS}} + \Theta^{\mathrm{HS}}}$$

$\Theta^{\mathrm{HS}} = 0.0$

Θ^{BS}	0.000	-0.313	-1.250	-2.813	-5.000
c	0.200	0.185	0.143	0.079	0.000
$S^{\alpha\beta}$	0.00	0.25	0.50	0.75	1.00
Δr(Fe–Fe) [Å]	0.000	0.004	0.015	0.033	0.054
Δr(Fe–S) [Å]	0.000	0.002	0.007	0.016	0.025
ΔJ [cm^{-1}]	0	9	33	69	110