Thermodynamic Aspects of Magnetic Molecules

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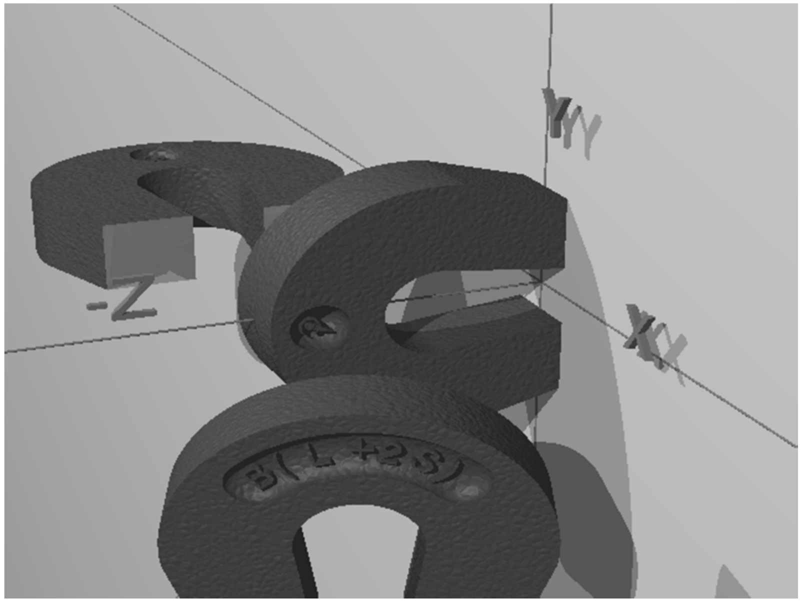

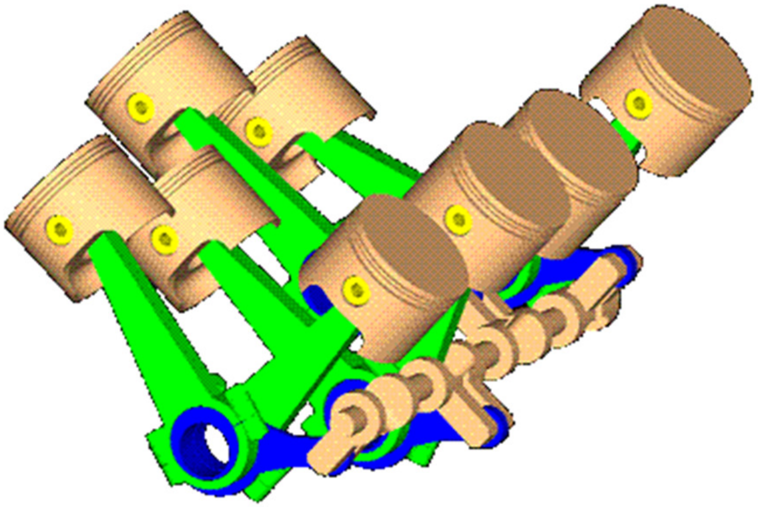

San Francisco, Dec 1, 2014

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OPTIMAS

Outlook

- Introduction
  - Hamiltonian
  - Basics of quantum thermodynamics
- Understanding QTD
  - Z system
  - Doublet harmonic oscillator
- Results
  - Otto cycle and magnetism
  - Diesel cycle and magnetism
- Summary

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Degrees of Freedom in the Hamiltonian

$$\hat{H}^{(0)} = -\frac{1}{2}\sum_{i=1}^{N_{\rm el}}\nabla^2 - \sum_{i=1}^{N_{\rm el}}\sum_{a=1}^{N_{\rm at}}\frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} + \sum_{i=1}^{N_{\rm el}}\sum_{j=1}^{N_{\rm el}}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{a=1}^{N_{\rm at}}\sum_{b=1}^{N_{\rm at}}\frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$

electronic
correlations

$$\hat{H}^{(1)} = \sum_{i=1}^{N_{el}}\frac{Z_a^{\rm eff}}{2c^2 R_i^3}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} + \sum_{i=1}^{N_{\rm el}}\mu_L\hat{\mathbf{L}}\cdot\mathbf{B} + \sum_{i=1}^{N_{\rm el}}\mu_S\hat{\mathbf{S}}\cdot\mathbf{B} + \sum_{i=1}^{N_{\rm el}}\sum_{\mathbf{q}}\lambda_i^{\mathbf{q}}\langle\mathbf{q}\rangle$$

SOC static B-field phonons

$$\hat{H}^{(2)}(t) = \hat{\mathbf{d}}^{(0+1)}\cdot\mathbf{E}_{laser}(t) + \hat{\mathbf{M}}^{(0+1)}\cdot\mathbf{B}_{laser}(t)$$

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}^{(2)}(t)|\Psi(t)\rangle$$

laser

$$\rho(T) = \frac{1}{Z(T)}\sum_i |i\rangle\langle i| e^{-E_i\beta}$$

temperature

Electronic Correlations in the Hamiltonian

$$\hat{H}^{(0)} = -\frac{1}{2}\sum_{i=1}^{N_{\mathrm{el}}}\nabla^2 - \sum_{i=1}^{N_{\mathrm{el}}}\sum_{a=1}^{N_{\mathrm{at}}}\frac{Z_a}{|\mathbf{R}_a - \mathbf{r}_i|} + \sum_{i=1}^{N_{\mathrm{el}}}\sum_{j=1}^{N_{\mathrm{el}}}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{a=1}^{N_{\mathrm{at}}}\sum_{b=1}^{N_{\mathrm{at}}}\frac{Z_a Z_b}{|\mathbf{R}_a - \mathbf{R}_b|}$$

$\{\phi_1(\boldsymbol{r}), \phi_2(\boldsymbol{r}), \cdots, \phi_n(\boldsymbol{r})\}$ occupied

$\{\phi_{n+1}(\boldsymbol{r}), \phi_{n+2}(\boldsymbol{r}), \cdots, \phi_{N_{\mathrm{b.f.}}}(\boldsymbol{r})\}$ virtual

Configuration interaction or coupled cluster expansion

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_n) = \frac{1}{\sqrt{n!}}\left(C_0 \begin{vmatrix} \phi_1(\boldsymbol{r}_1) & \phi_2(\boldsymbol{r}_1) & \cdots & \phi_n(\boldsymbol{r}_1) \\ \phi_1(\boldsymbol{r}_2) & \phi_2(\boldsymbol{r}_2) & \cdots & \phi_n(\boldsymbol{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\boldsymbol{r}_n) & \phi_2(\boldsymbol{r}_n) & \cdots & \phi_n(\boldsymbol{r}_n) \end{vmatrix} + \sum_{\substack{a\in\mathrm{Virt} \\ k\in\mathrm{Occ}}} C_k^a \begin{vmatrix} \phi_1(\boldsymbol{r}_1) & \cdots & \phi_a(\boldsymbol{r}_1) & \cdots & \phi_n(\boldsymbol{r}_1) \\ \phi_1(\boldsymbol{r}_2) & \cdots & \phi_a(\boldsymbol{r}_2) & \cdots & \phi_n(\boldsymbol{r}_2) \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \phi_1(\boldsymbol{r}_n) & \cdots & \phi_a(\boldsymbol{r}_n) & \cdots & \phi_n(\boldsymbol{r}_n) \end{vmatrix} \right.$$

$$\left. + \sum_{\substack{a,b\in\mathrm{Virt} \\ k,l\in\mathrm{Occ}}} C_{k,l}^{a,b} \begin{vmatrix} \phi_1(\boldsymbol{r}_1) & \cdots & \phi_a(\boldsymbol{r}_1) & \cdots & \phi_b(\boldsymbol{r}_1) & \cdots & \phi_n(\boldsymbol{r}_1) \\ \phi_1(\boldsymbol{r}_2) & \cdots & \phi_a(\boldsymbol{r}_2) & \cdots & \phi_b(\boldsymbol{r}_2) & \cdots & \phi_n(\boldsymbol{r}_2) \\ \vdots & \ddots & \vdots & \ddots & \vdots & \ddots & \vdots \\ \phi_1(\boldsymbol{r}_n) & \cdots & \phi_a(\boldsymbol{r}_n) & \cdots & \phi_b(\boldsymbol{r}_n) & \cdots & \phi_n(\boldsymbol{r}_n) \end{vmatrix} + \cdots \right)$$

Slater-rules → $\rho_{i,j}$ → $\langle\hat{O}\rangle$ & Mulliken analysis (localization)

Otto Cycle

Eugenio Barsanti and Felice Matteucci

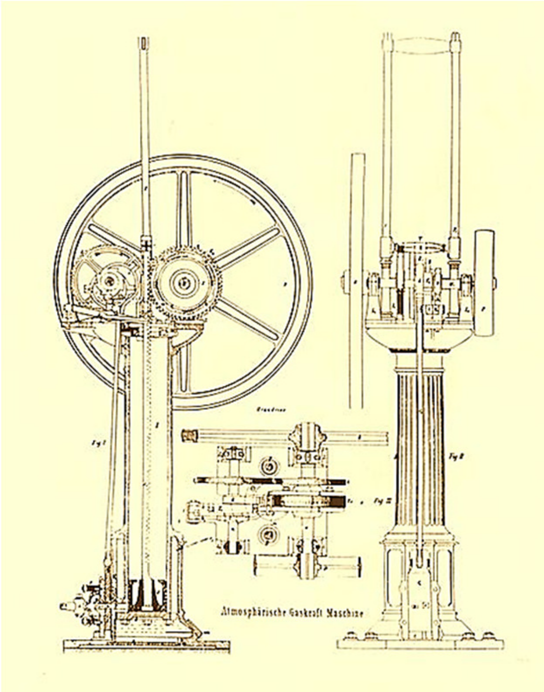
patented around 1854-1857

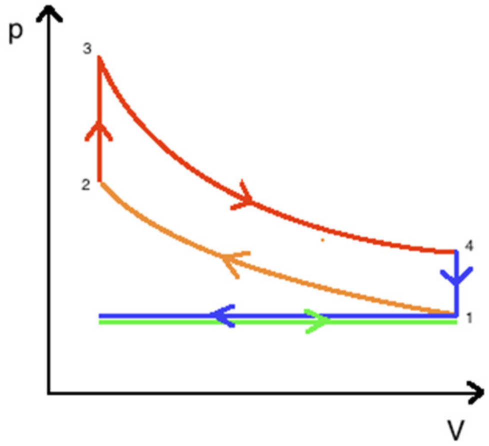
Alphonse Beau de Rochas

patented 1861

Nicolaus Otto

built 1863



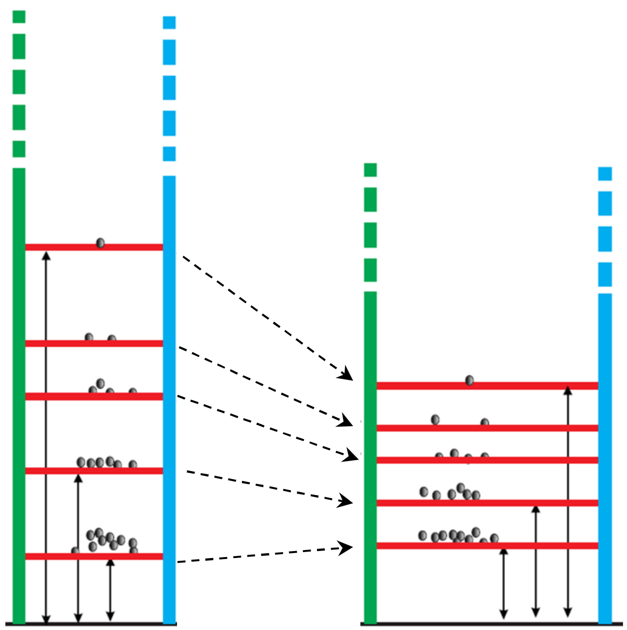


1→2 isentropic compression
2→3 isochoric heating
3→4 isentropic expansion
4→1 isochoric cooling (exhaust +intake)

Basics of Quantum Thermodynamics

$$U = \sum_n p_n E_n$$

- quantum levels: $\{E_n\} \rightarrow \{E_n'\}$
- occupations: $\{p_n\}$



- **quantum** first law of thermodynamics
  - internal energy $dU = \sum_n (E_n dp_n + p_n dE_n)$
  - **work** $dW = \sum_n p_n dE_n$
  - heat $dQ = \sum_n E_n dp_n$
  - volume L (1D system)
  - pressure $F = -\sum_n p_n \frac{dE_n}{dL}$

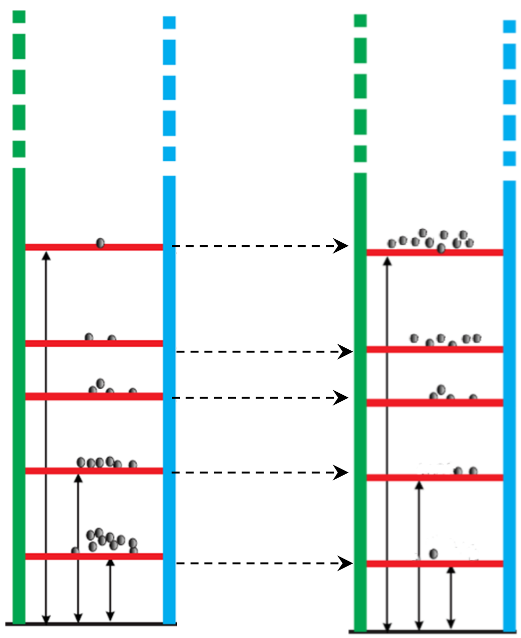
changing only E_n:
quantum adiabatic process

H. T. Quan, Y.-X. Liu, C. P. Sun, and F. Nori, Phys. Rev. B **76**, 031105 (2007)

Basics of Quantum Thermodynamics

$$U = \sum_n p_n E_n$$

- quantum levels: $\{E_n\}$
- occupations: $\{p_n\} \rightarrow \{p'_n\}$



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changing only p_n:
Heating/cooling

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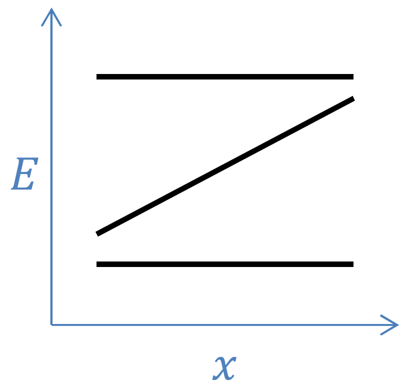
Z System



$|u\rangle$ E_u

$|e\rangle$ $E_e = ax + \Delta$

$|g\rangle$ $E_g = 0$

$$p_u(x,T) = \frac{e^{-\frac{E_u}{KT}}}{1+e^{-\frac{ax+\Delta}{KT}}+e^{-\frac{E_u}{KT}}} = \frac{e^{-E_u\beta}}{Z(x,T)}$$

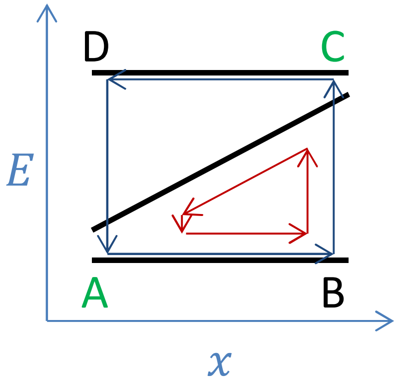
$$p_e(x,T) = \frac{e^{-\frac{ax+\Delta}{KT}}}{1+e^{-\frac{ax+\Delta}{KT}}+e^{-\frac{E_u}{KT}}} = \frac{e^{-E_e\beta}}{Z(x,T)}$$

$$p_g(x,T) = \frac{1}{1+e^{-\frac{ax+\Delta}{KT}}+e^{-\frac{E_u}{KT}}} = \frac{1}{Z(x,T)}$$

$E_{\text{tot}} = p_e(x_1,T_1)E_e(x_2)+p_u(x_1,T_1)E_u(x_2)$

thermalization if $x_1 = x_2$

Z System



$|u\rangle$ E_u

$|e\rangle$ $E_e = ax + \Delta$

$|g\rangle$ $E_g = 0$

$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} < 1$$

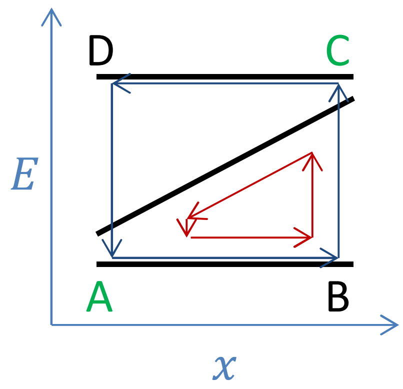
$$E_A = p_e(x_1, T_1)E_e(x_1) + p_u(x_1, T_1)E_u$$
$$E_B = p_e(x_1, T_1)E_e(x_2) + p_u(x_1, T_1)E_u$$
$$E_C = p_e(x_2, T_2)E_e(x_2) + p_u(x_2, T_2)E_u$$
$$E_D = p_e(x_2, T_2)E_e(x_1) + p_u(x_2, T_2)E_u$$

$$Q_{\text{in}} = [p_e(x_2, T_2) - p_e(x_1, T_1)]E_e(x_2) + [p_u(x_2, T_2) - p_u(x_1, T_1)]E_u$$
$$Q_{\text{out}} = [p_e(x_2, T_2) - p_e(x_1, T_1)]E_e(x_1) + [p_u(x_2, T_2) - p_u(x_1, T_1)]E_u$$

useful work produced by $|e\rangle$
maximized near (not at)
crossing/degeneracy

useless energy-move-around due to $|u\rangle$
minimized if $p_u(x_2, T_2) = p_u(x_1, T_1)$
→**gap+finite temperature**

Z System



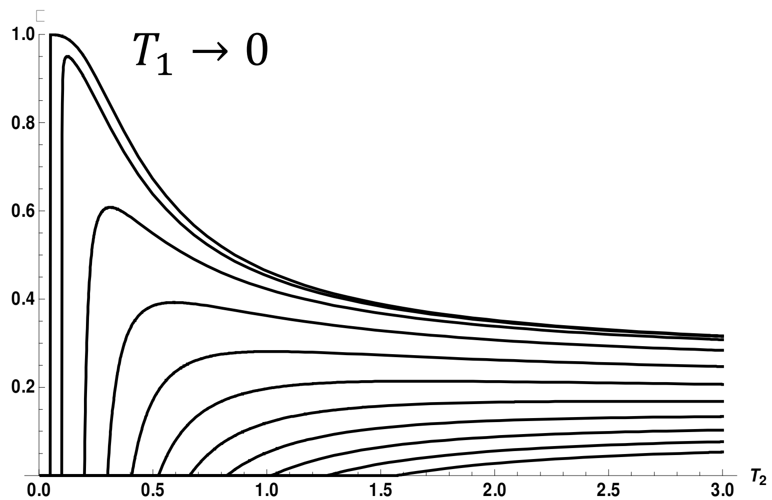
$|u\rangle \qquad E_u$

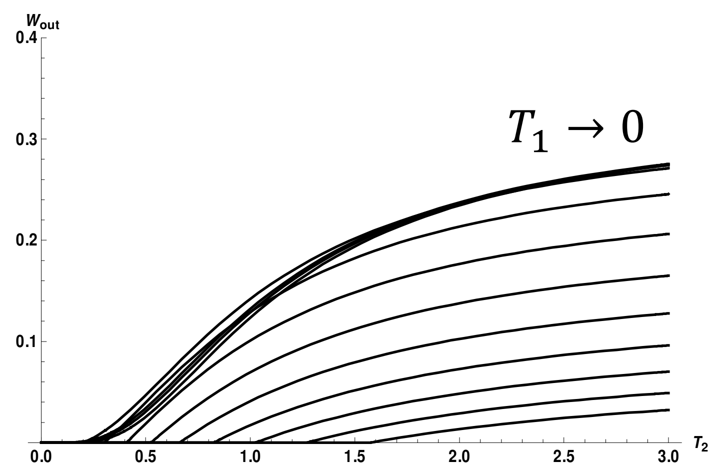
$|e\rangle \qquad E_e = ax + \Delta$

$|g\rangle \qquad E_g = 0$

$$\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} < 1$$

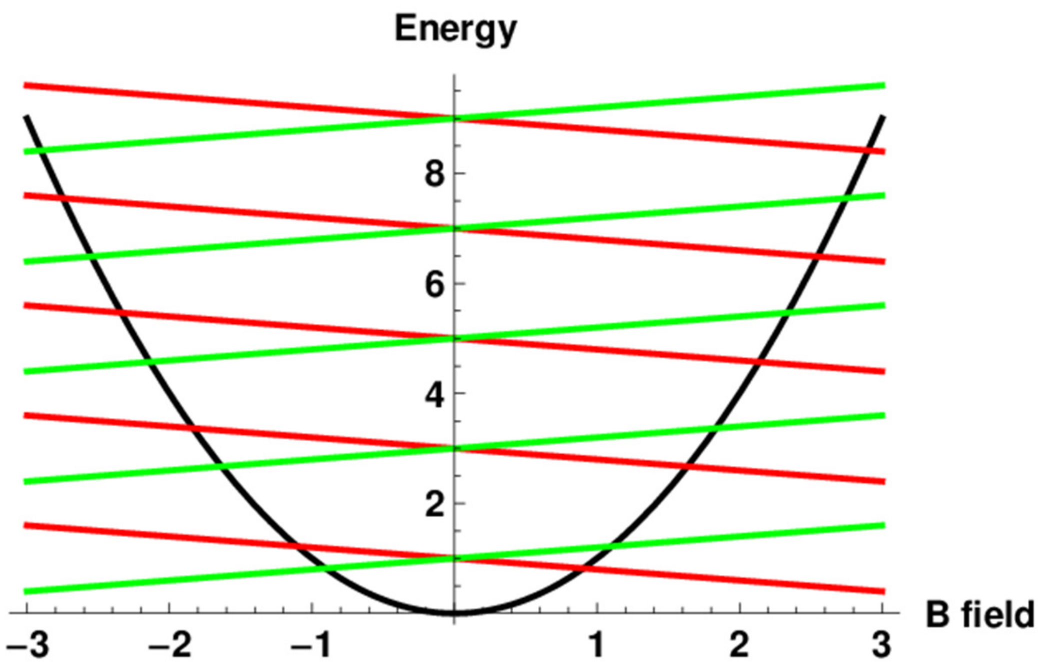
$$\eta = \frac{[p_e(x_2,T_2) - p_e(x_1,T_1)][E_e(x_2) - E_e(x_1)]}{[p_e(x_2,T_2) - p_e(x_1,T_1)]E_e(x_2) + [p_u(x_2,T_2) - p_u(x_1,T_1)]E_u}$$





For $T_1 \to 0$ and very small ΔT we get $\eta \to 1$ but **very little energy conversion per cycle**. At room temperature we get $\eta \to 0.3$

Doublet Harmonic Oscillator



Spin up $E_n^- = \left(\frac{1}{2} + n\right)\omega + \mu B$

Spin down $E_n^+ = \left(\frac{1}{2} + n\right)\omega - \mu B$

$$Z = \sum_{n=1}^{\infty} \exp\left(-\frac{E_n^+}{KT}\right) + \sum_{n=1}^{\infty} \exp\left(-\frac{E_n^-}{KT}\right) = \exp\left(-\frac{\omega}{KT}\right)\cosh\left(\frac{\mu B}{KT}\right)\operatorname{csch}\left(\frac{\omega}{2KT}\right)$$

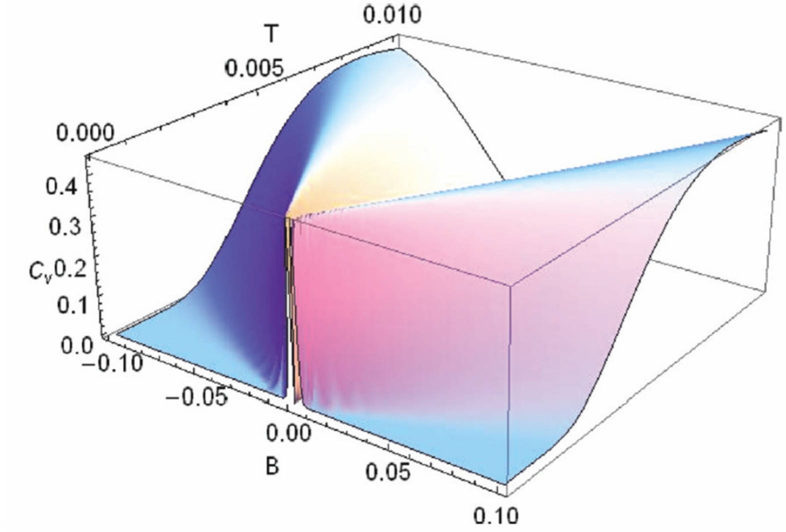
$$\mathrm{E} = \frac{1}{Z}\left\{\sum_{n=1}^{\infty} E_n^+ \exp\left(-\frac{E_n^+}{KT}\right) + \sum_{n=1}^{\infty} E_n^- \exp\left(-\frac{E_n^-}{KT}\right)\right\} = \omega + \frac{\omega}{2}\coth\left(\frac{\omega}{2KT}\right) - \mu B \tanh\left(\frac{\mu B}{KT}\right)$$

C. D. Dong, G. Lefkidis and W. Hübner, Phys. Rev. B **88**, 214421 (2013)

Doublet Harmonic Oscillator

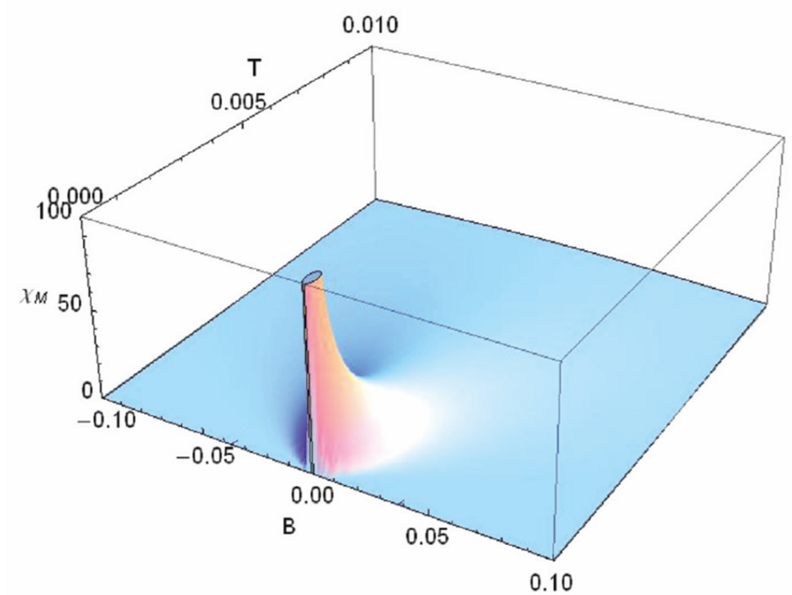
Heat capacity

$$C_v = \frac{\partial E(T,B,\omega)}{\partial T}$$
$$= \frac{1}{4KT^2}\left[\omega^2 \operatorname{csch}^2\left(\frac{\omega}{2KT}\right) + 4\mu^2 B^2 \operatorname{sech}^2\left(\frac{\mu B}{KT}\right)\right]$$



Magnetic susceptibility

$$\chi_M = \frac{\partial}{\partial B}\left\{\frac{1}{2Z}\sum_{n=1}^{\infty}\exp\left(-\frac{E_n^+}{KT}\right) - \frac{1}{2Z}\sum_{n=1}^{\infty}\exp\left(-\frac{E_n^-}{KT}\right)\right\}$$
$$= \frac{\mu \operatorname{sech}^2\left(\frac{\mu B}{KT}\right)}{2KT}$$



C. D. Dong, G. Lefkidis and W. Hübner, Phys. Rev. B **88**, 214421 (2013)

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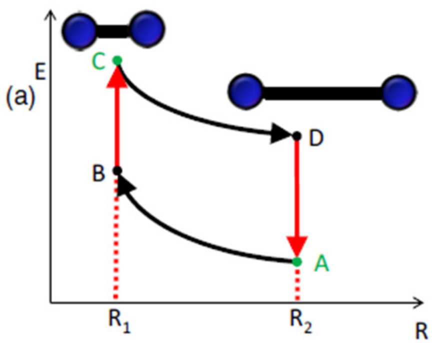
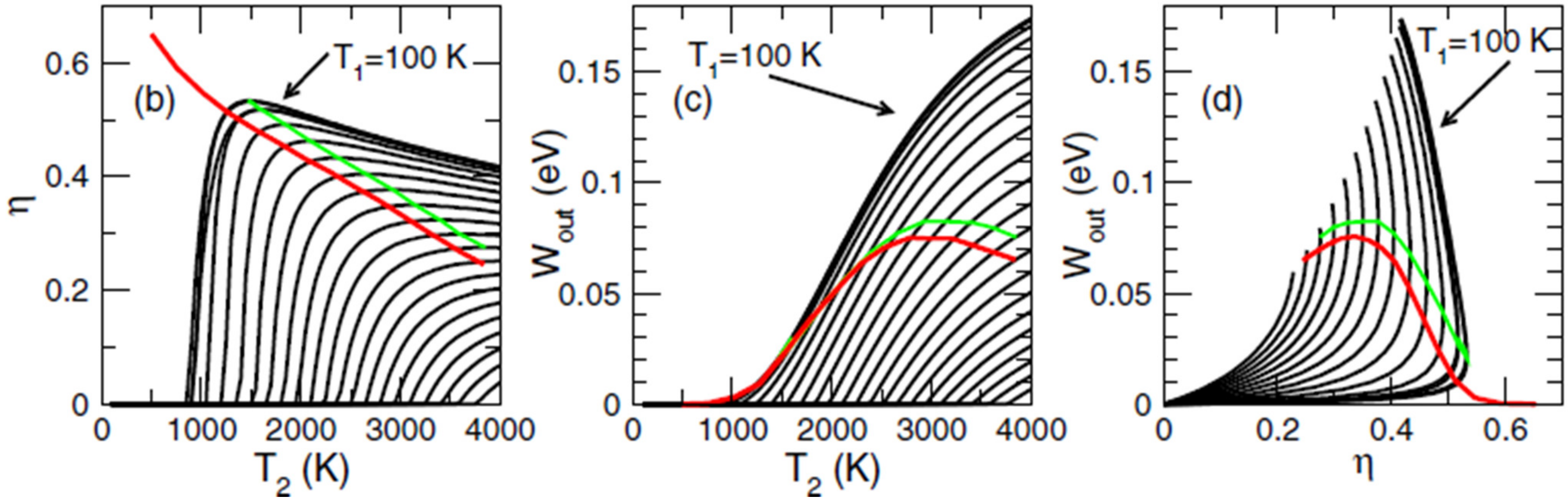
Otto Cycle on Ni_2: Efficiency and Work Output

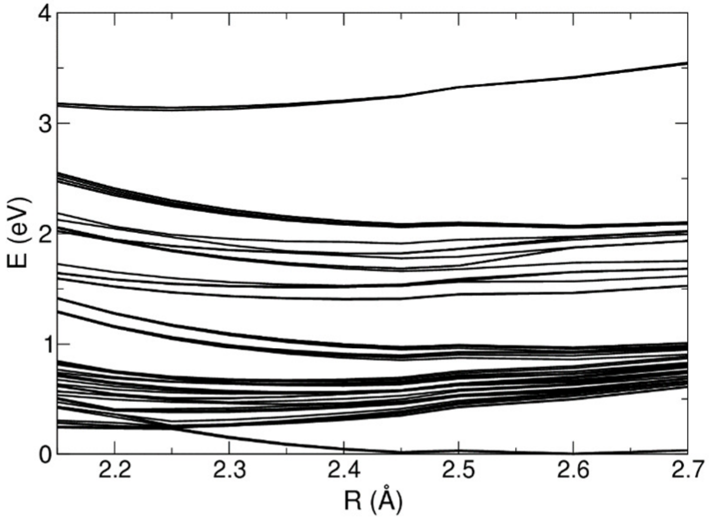


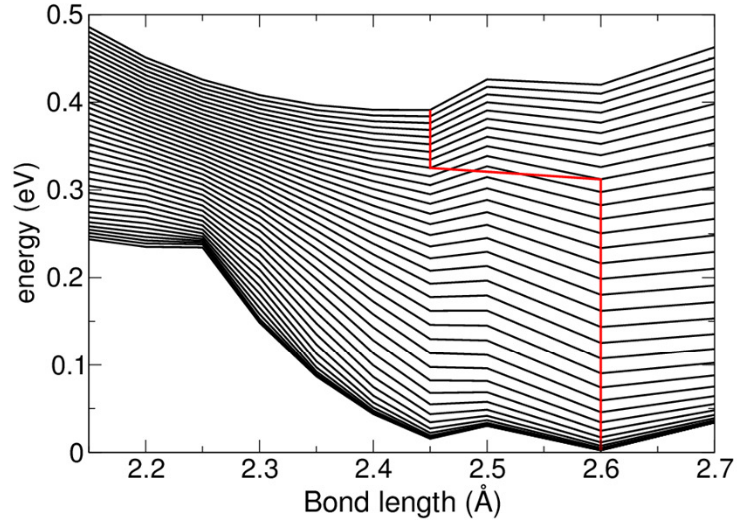
- Magnetism increases output power at maximum efficiency
- Magnetism increases work output

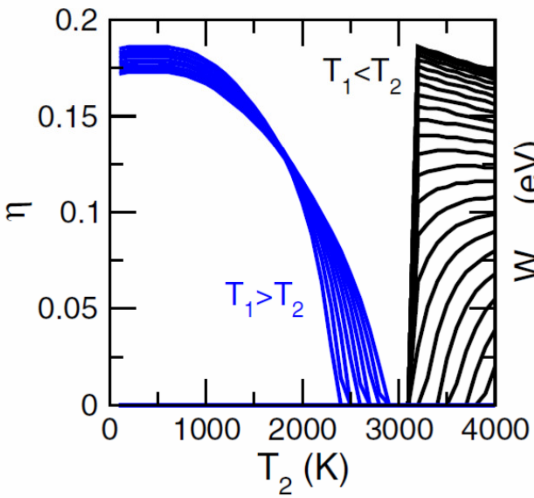


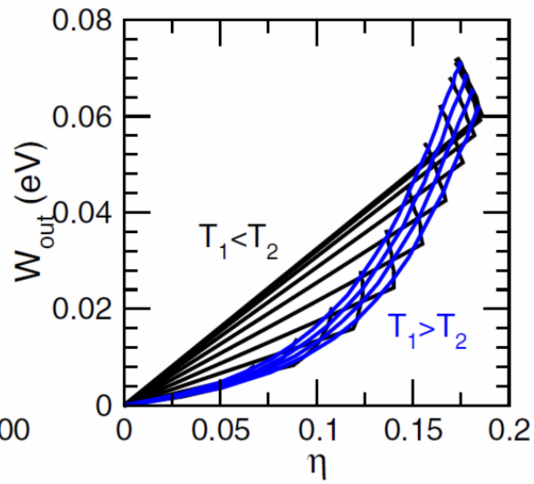
W. Hübner, G. Lefkidis, C. D. Dong, D. Chaudhuri, L. Chotorlishvili, and J. Berakdar
Phys. Rev. B **90**, 024401 (2014)

Otto Cycle on Ni_2: Equilibrium Distance









Only molecules can both expand and compress spontaneously!

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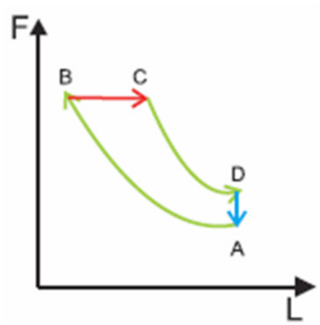
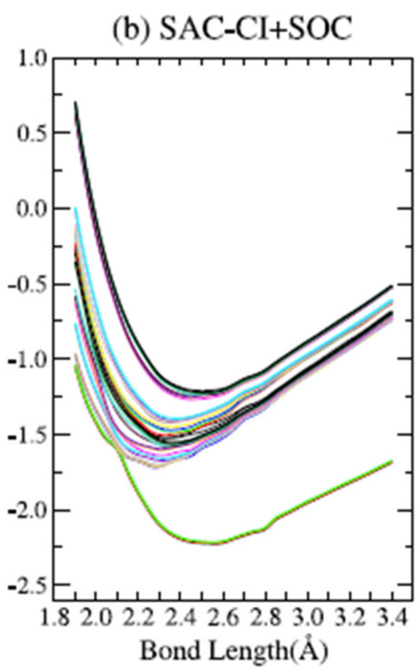
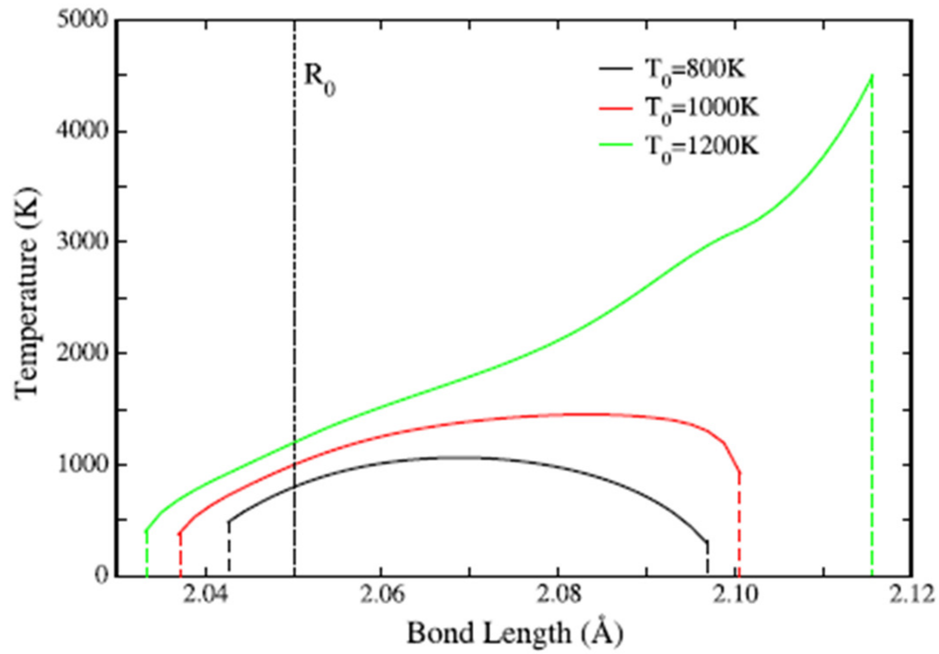
Phys. Rev. B **90**, 024401 (2014)

Diesel Cycle on Ni_2: Isobaric Process in Ni_2





Isobaric ranges



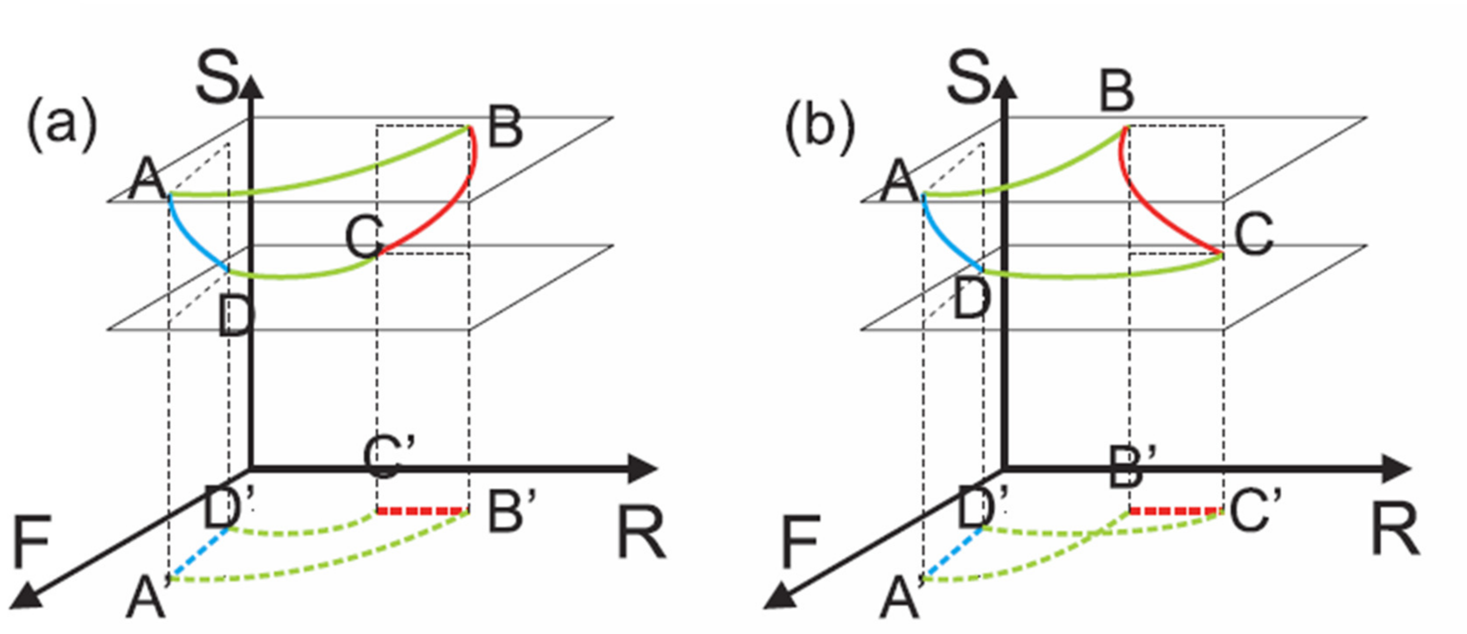
$$F(R,T) = -\frac{1}{Z(R,T)}\sum_i \frac{dE_i(R)}{dR} e^{-\frac{E_i(R)}{KT}}$$

Non-equilibrium, non-thermalized states!

C. D. Dong, G. Lefkidis and W. Hübner, J. Supercond. Nov. Magn. **26**, 1589 (2013)

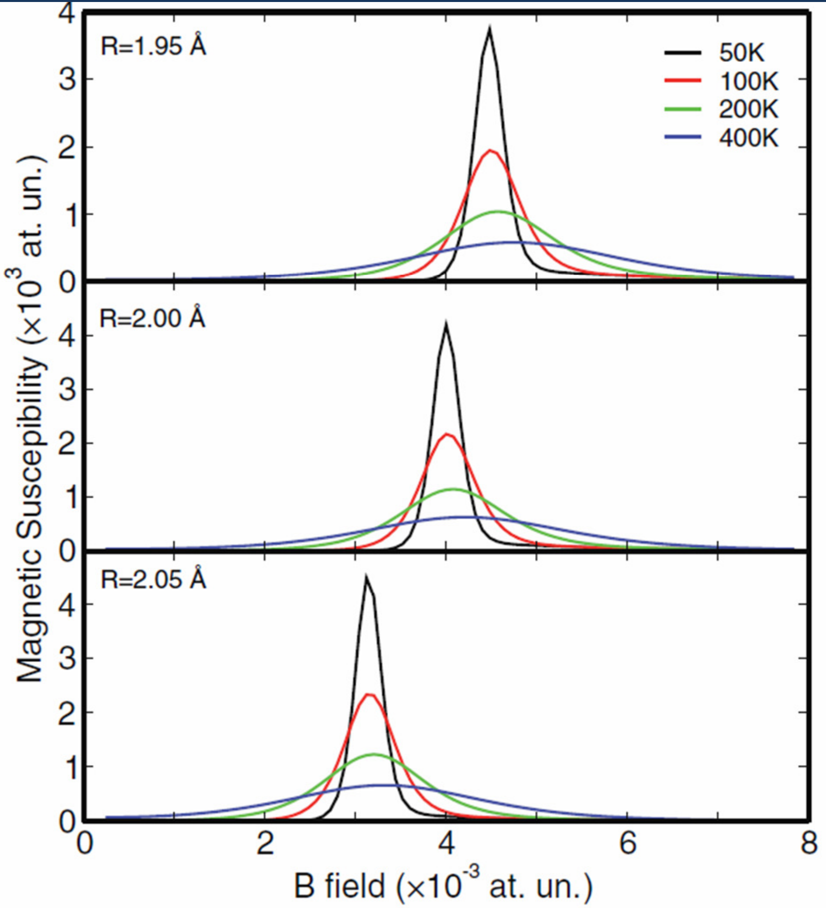
Entropy and Quantum Thermodynamics

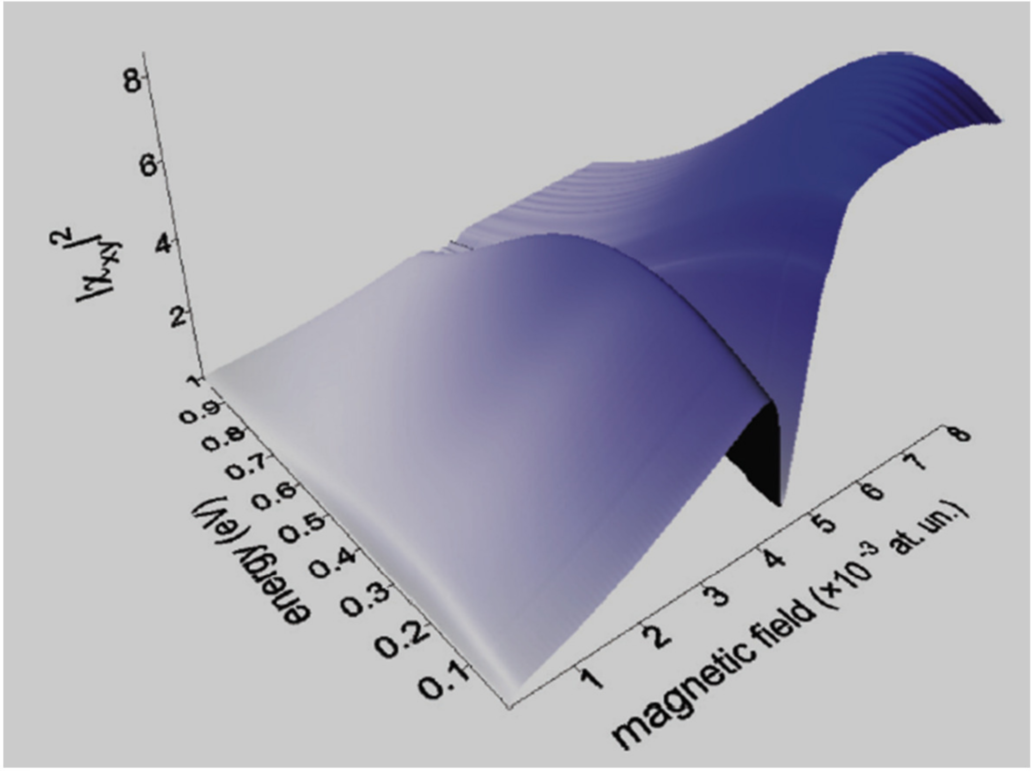
Entropy: $S = -k \sum_i p_i \ln p_i$



- Crossings of lines in PV diagrams due to additional degrees of freedom
- Even larger configuration space for magnetic molecules

Heat Capacity and Magnetic Susceptibility of Ni_2





$$\chi_M = \frac{\partial \langle M(T,R) \rangle}{\partial B}$$

$$\chi_{ij}^{(xy)} \propto \sum_k \left(D_{ik}^{(x)}\right)^* D_{kj}^{(y)} \frac{p_i - p_j}{E_i - E_j - \omega + i\Gamma}$$

Singularities indicate level crossings.

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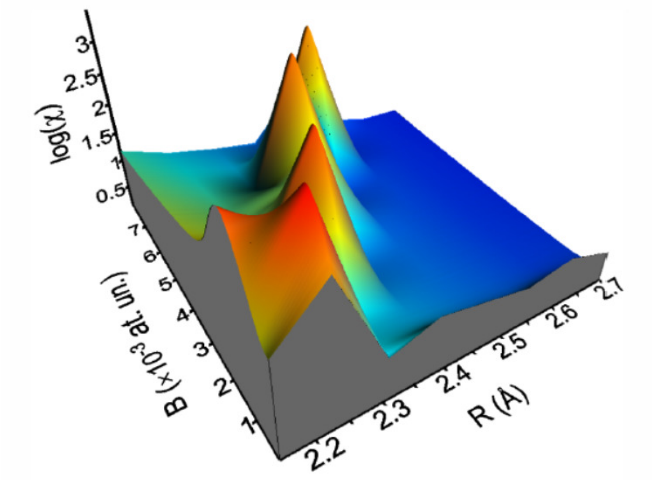
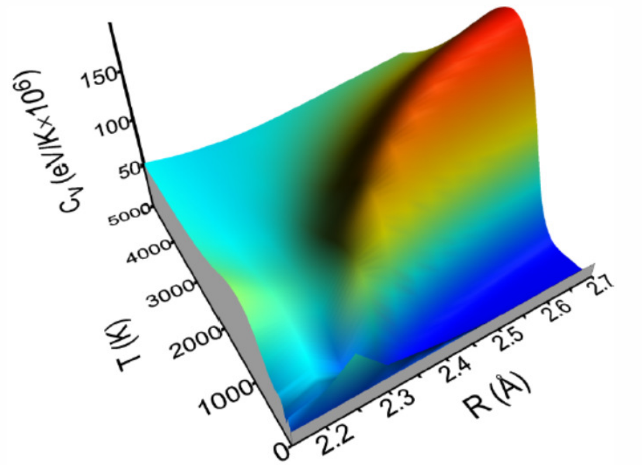
Heat Capacity and Magnetic Susceptibility of Ni_2

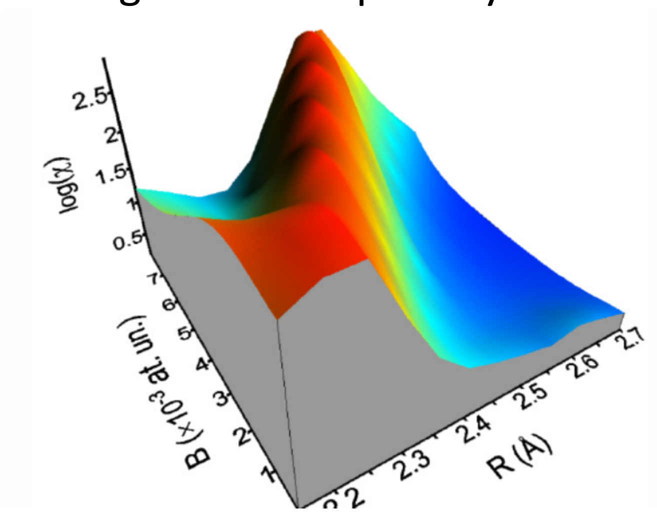
Magnetic susceptibility at 100 K



Heat capacity

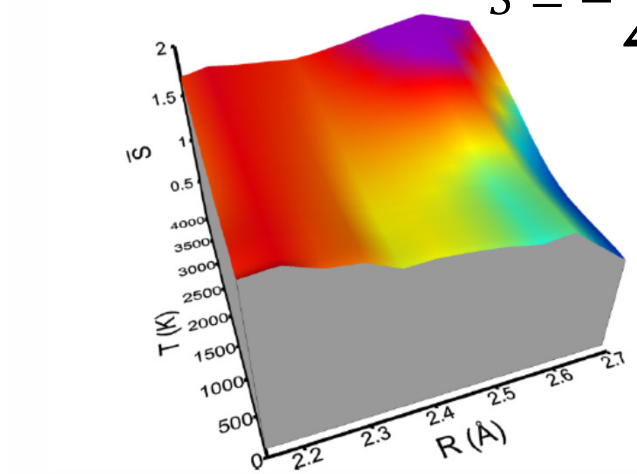


Magnetic susceptibility at 400 K



Von-Neumann entropy

$$\bar{S} = -\sum_{ni} p_n \mathrm{Tr}\left(\rho_n^{(red)} \ln \rho_n^{(red)}\right)$$



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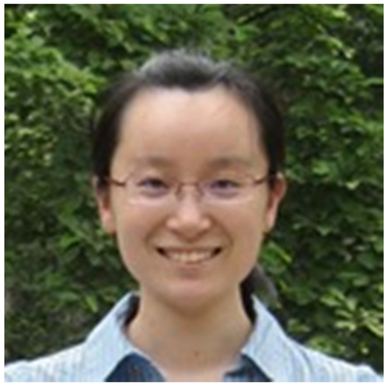
Summary

- QTD: Effects of energy discretization (in particular level crossings)
- Electronic temperature – non thermalized states
- Quantum Otto Cycle – effects of magnetism
- Isobaric process – Quantum Diesel Cycle

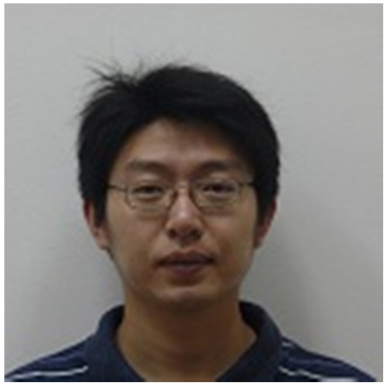
Acknowledgements

Wei Jin (Xi'an)



Hongping Xiang (Northridge)

Chuanding Dong



Debapriya Chaudhuri

Chun Li (Xi'an)

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ZEISS

We make it visible.