

Knowledge discovery using data mined from Nuclear Magnetic Resonance spectral images

William J Brouwer¹, Saurabh Kataria², Prasenjit Mitra², Karl Mueller¹, C. Lee Giles²

*¹Department of Chemistry, ²Department of Information Sciences and Technology,
Pennsylvania State University, University Park PA 16802*

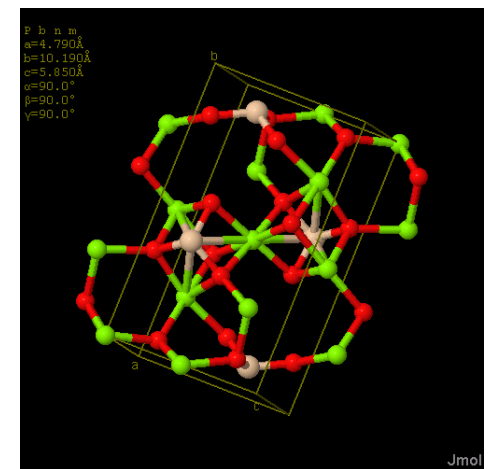
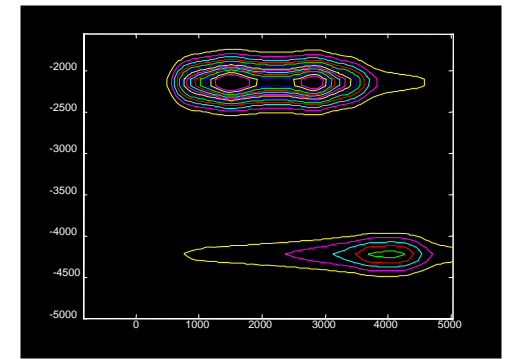


CHE- 0535656



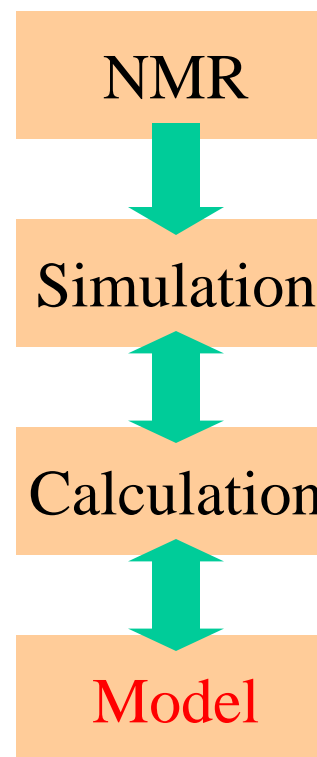
Outline

- Motivation
 - Structure determination
 - Invoking + building cyberinfrastructure
- Method
 - Solid State *ab initio* calculations
 - Nuclear Magnetic Resonance (NMR)
 - Support Vector Machines (SVM) + NMR
- Results
 - High Resolution experiment + Ensemble SVM
- Future Work
 - Sequestration
 - Surface science
- Conclusions

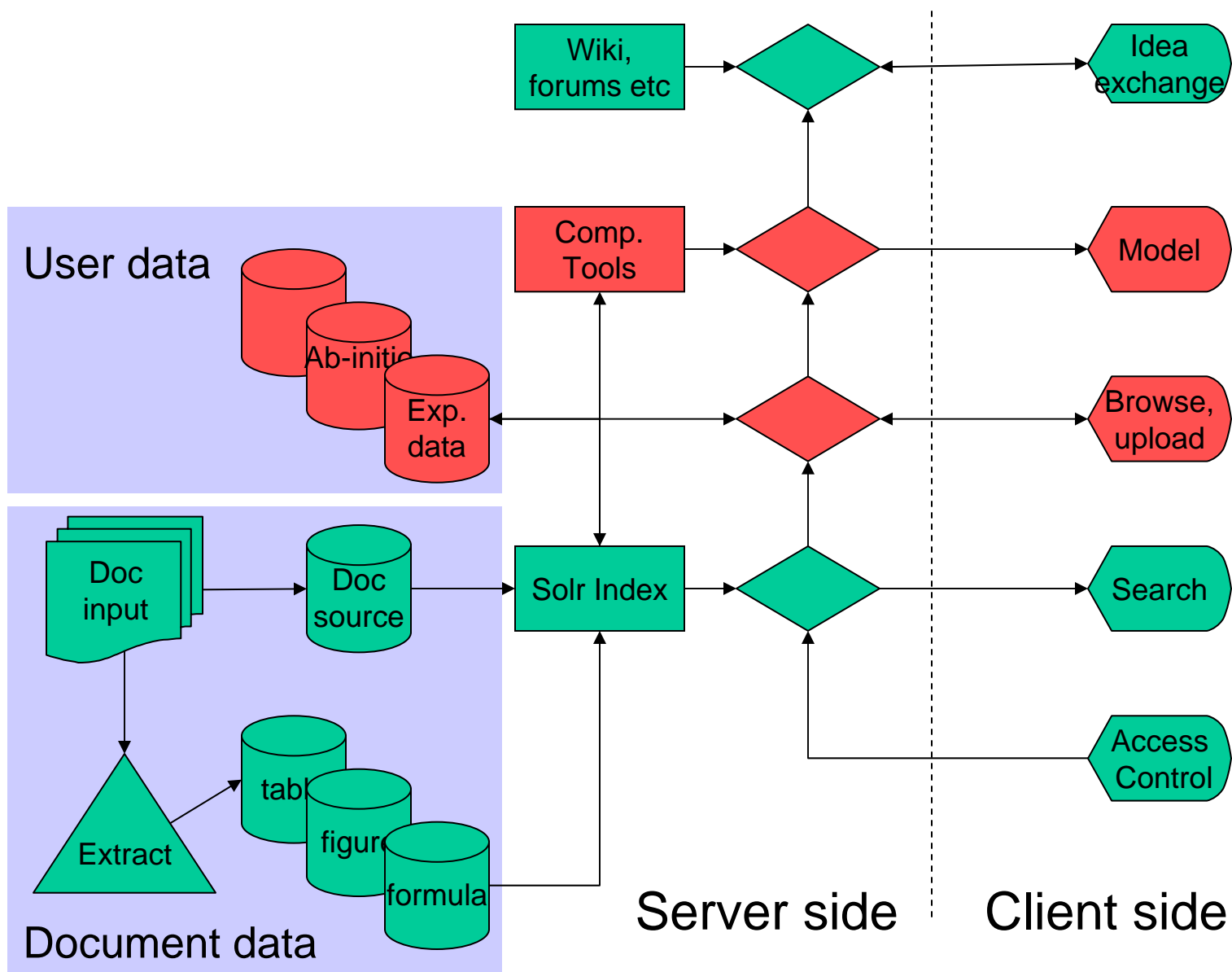


Motivation

- Solid State NMR is powerful local probe of atomic structure
 - Local geometry; bond angles, lengths
 - Local chemical identity (eg., steric differences directly influence local bonds etc)
- NMR Lineshapes often complicated by broadening mechanisms, *interpretation requires intensive work including simulation, ab initio and/or empirical calculations*
- Machine Learning (ML) promises to reduce the burden of interpretation by *removing* intermediate steps
- Requires voluminous *data*, such as that provided by cyberinfrastructure, eg., Chem_xSeer -> <http://chemxseer.ist.psu.edu/>

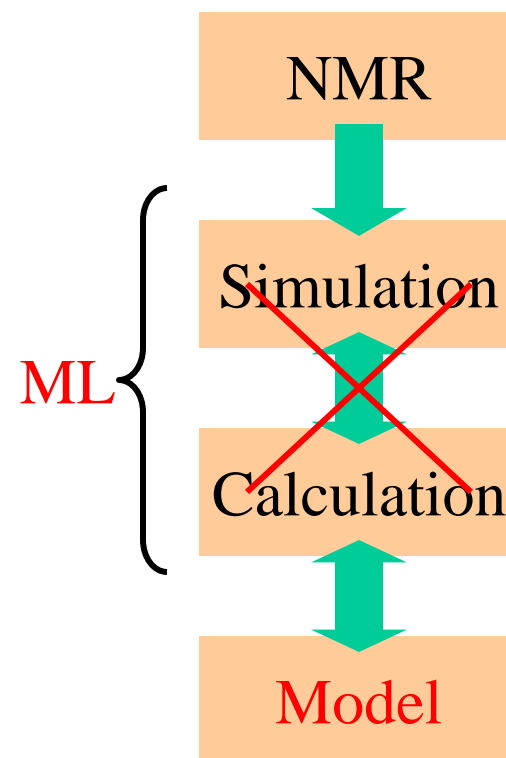


The Chem_xSeer Collaboratory



Method

- Collaboratories bridge divides imposed by resources, geography to create a distributed research environment
- Chem_xSeer provides access to digital libraries and allows end-users to search using unique features such as tables, figures as well as text from documents
- *Using data from Chem_xSeer, an end-user may employ machine learning to determine structural models for NMR spectra of novel materials*
- The focus of this work is on using data from *ab initio* calculations and simulations of NMR spectra, to train support vector machines, to be used for structure determination



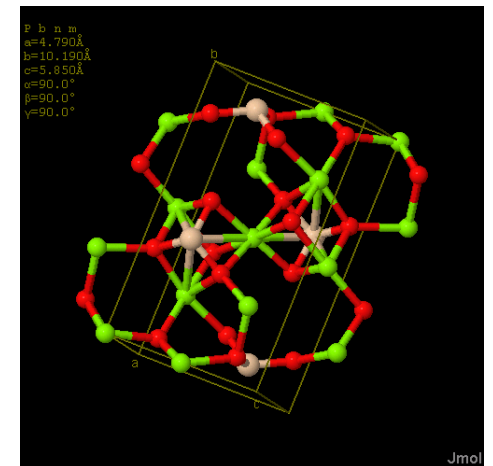
Solid State *Ab Initio*

- Solve Schrodinger (many body) equation with approximations eg., Born-Oppenheimer, Kohn-Sham DFT, to find *electronic wave functions* ϕ , given input structure/unit cell:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + u_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{xc}[\rho] \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

- Use plane wave (PW) expansions + pseudopotentials for core regions, accounting for full crystal periodicity.
- Can also relax structure ie., find optimal atomic positions by minimizing forces between atoms
- Goal of *ab initio* methods is to calculate physical properties we may measure by some experimental method

Forsterite Unit Cell



Example: Forsterite

- Construct pseudopotentials for Si,O,Mg eg., for Mg pseudize core of $1s^2 2s^2 2p^6$, valence orbitals $3s^2 3p^0 3d^0$ treated with Projector Augmented Waves (PAW)
- Using refined (and/or relaxed) structure, perform Self-Consistent Field calculation for electronic structure, using DFT
- Resultant wave functions ψ take into account full system periodicity, *may be used to calculate expectation values of electric field gradient tensor \mathbf{V} measurable in solid state NMR via the quadrupole coupling constant C_q and asymmetry parameter η :*

$$V_{zz} = \langle \psi | \mathbf{V}_{zz} | \psi \rangle;$$

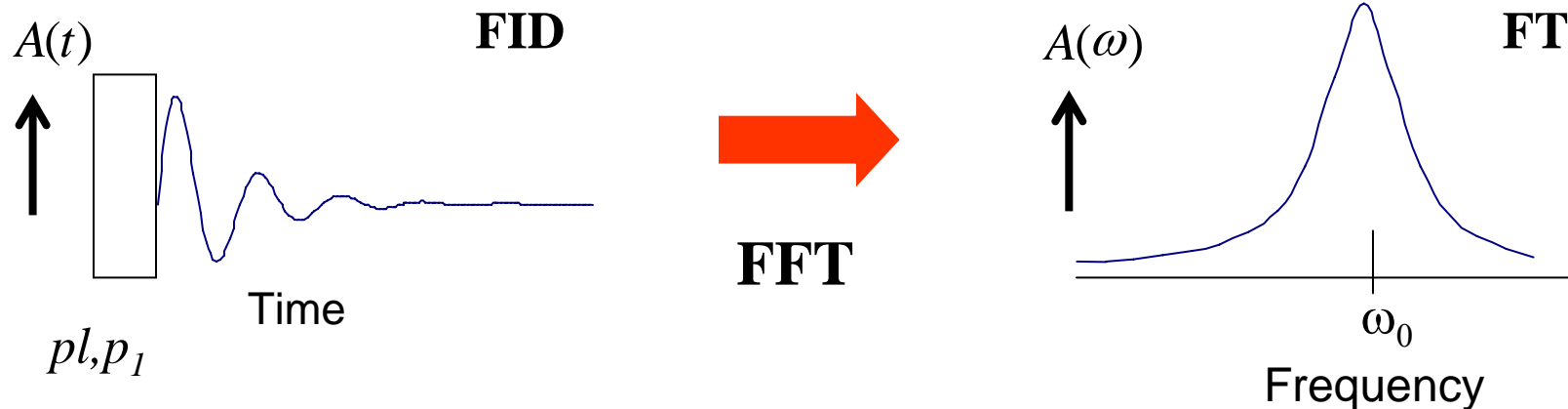
$$V_{yy} = \langle \psi | \mathbf{V}_{yy} | \psi \rangle;$$

$$V_{xx} = \langle \psi | \mathbf{V}_{xx} | \psi \rangle$$

$$C_q = \frac{e^2 V_{zz} Q}{\hbar}; \eta = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

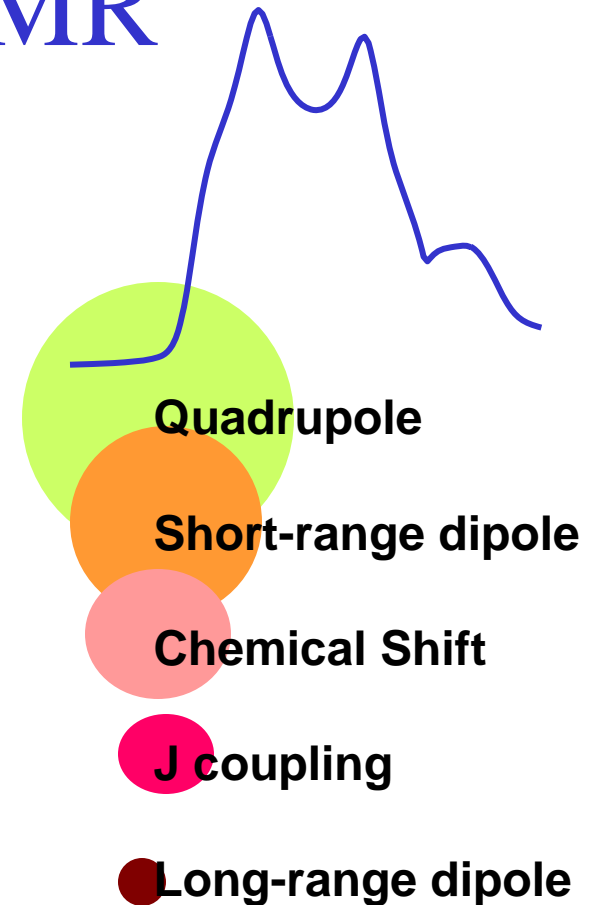
Solid State NMR (SS-NMR)

- Nuclei with non-zero spin I couple with static magnetic field \mathbf{B} to produce $2I+1$ Zeeman energy levels; nuclear spin precess at Larmor frequency ω_0
- Samples embedded in static \mathbf{B} field are pulsed with RF energy at \sim Larmor freq, with pulse duration p_l and power pl
- Time response is Free Induction Decay, Fourier transformed via FFT; **peak positions (shifts away from Larmor freq.) are functions of interactions and thus local structure...**



Interactions of NMR

- Vast majority of nuclei have spin $> \frac{1}{2}$ and thus quadrupole moment Q which couples with a surrounding electric field gradient, largest interaction
- In polycrystalline solids, this *quadrupole interaction* broadens NMR lines :
 - helpful b/c distinctive lineshapes give direct insight into local bonding arrangement
 - detrimental b/c promotes overlap between lines from distinct chemical environments & need to simulate
- Mitigate with Magic Angle Spinning (MAS), mechanical technique which on time average removes 1st order quadrupole broadening, but 2nd order effects remain...



Multiple Quantum MAS (MQMAS)

- Bary centers for quadrupole nuclei ($I > 1/2$) using MAS have an isotropic chemical and quadrupole shift, as well as an anisotropic term, which introduces broadening in polycrystalline materials, function of crystallite orientation α, β :

$$\omega_{r,c} = \underbrace{(r-c)\omega_0\delta_{cs}^{iso}}_{\text{Chemical shift}} - \underbrace{\frac{r-c}{\omega_0} \left[\frac{C_q}{2I(2I+1)} \right]^2}_{\text{2nd order quadrupole shift}} \left\{ \underbrace{A^{(0)}(I,r,c) \left(\frac{\eta^2+3}{10} \right) + A^{(4)}(I,r,c) f(\eta,\alpha,\beta)}_{\text{Anisotropic term}} \right\}$$

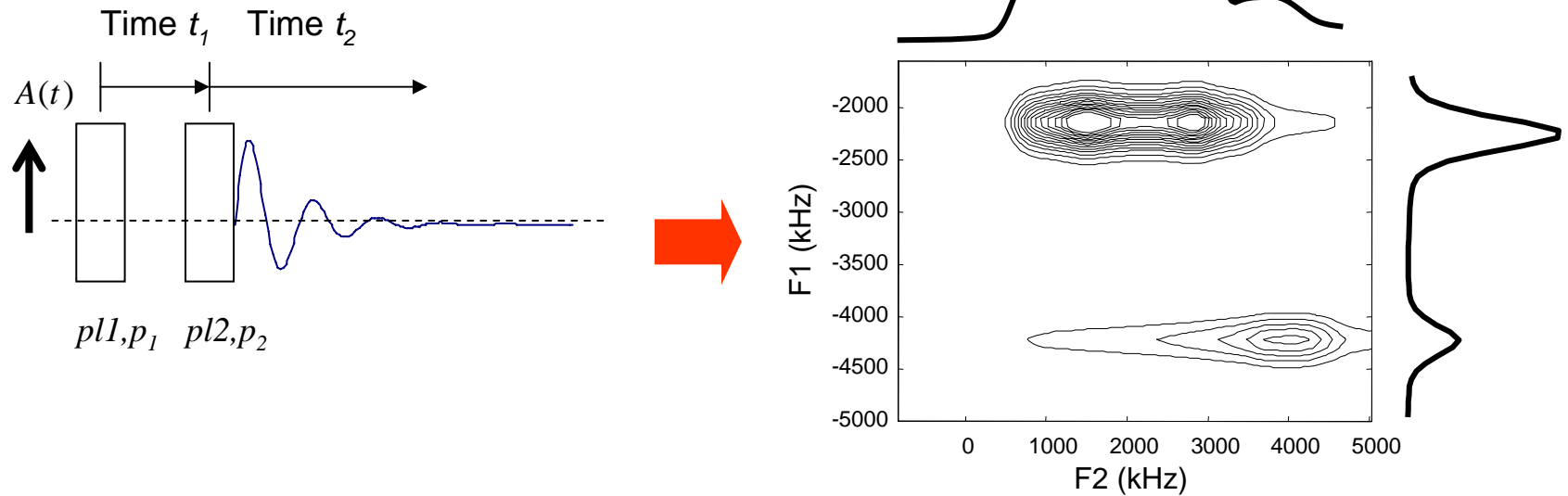
Chemical shift

2nd order quadrupole shift

Anisotropic term

- Can only detect coherences with change in magnetic quantum number (energy transitions) with $r-c = +/- 1$ (single quantum coherence)
- **MQMAS** -> acquire data in experiment as function of *two* independent time intervals, multiple quantum coherences detected indirectly (evolve btwn pulses)

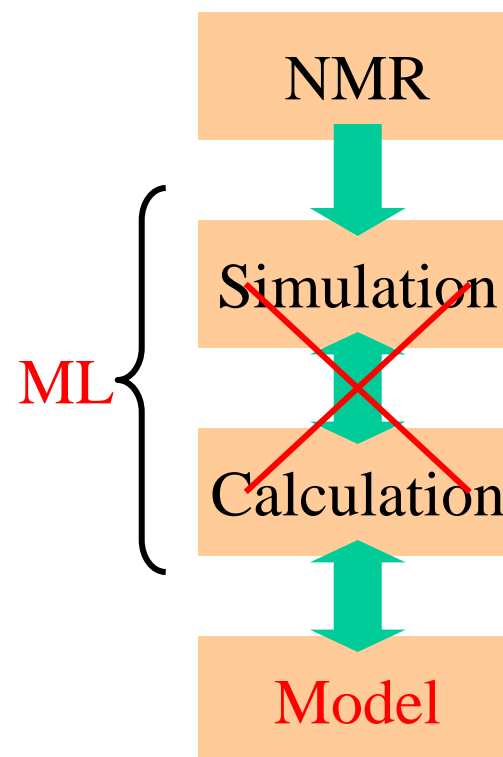
Example: ^{25}Mg MQMAS of Forsterite



- FFT in two dimensions, indirect dim is *isotropic*, by virtue of experimental details and/or data processing
- Two inequivalent Mg sites revealed as distinct NMR peaks, having specific values for asymmetry parameter η and quadrupole coupling constant C_q

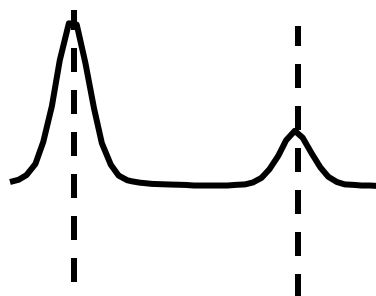
Machine Learning with SS-NMR data

- Comparison of parameters extracted via simulation of spectrum with *ab initio* results allows for unequivocal assignment
- Ideally would like to eliminate/reduce *ab initio* + simulation in order to do interpretation on SS-NMR spectra
- 2D data may exist as either image (eg., from article) or processed binary data from experiment
- In the former case, pixel data representing data easily maps to intensity *IF* contour levels are defined (eg., in figure caption)
 - contours don't overlap, use methods developed in ChemXSeer with heuristics + CCL to recreate data
 - Couple with document text and/or *ab initio* to provide corresponding structure for input spectra...

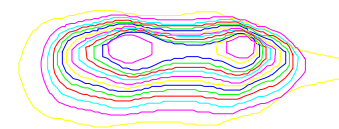


Features for Machine Learning

- Need position + intensity invariant features for ML



- Use isotropic dimension in MQMAS to locate peaks for distinct chemical sites
- Intensity data may be large and many in number eg., 200x100 frequency points = 20k features
- Use eigenvalues of Hessian scaled by relative intensities I to reduce dimensions/no. of features



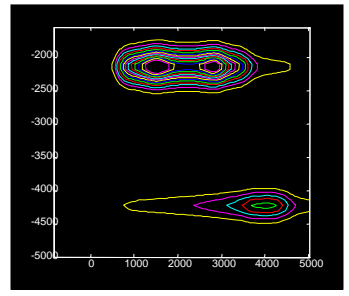
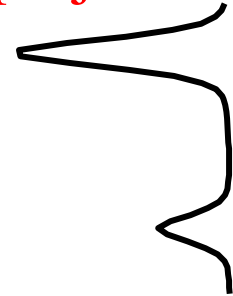
$$a = \begin{matrix} 3.12 & 3.15 & \dots & 2.97 \\ 3.15 & 3.17 & & 2.63 \\ \vdots & & & \vdots \\ 2.33 & 1.91 & \dots & 4.12 \end{matrix}$$



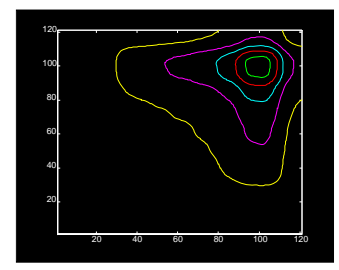
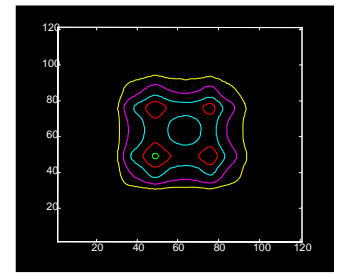
$$\lambda_j = \frac{I_j \cdot \text{eig}(a^T \cdot a)}{\sum_{j=1}^N I_j}$$

Example: Features from ^{25}Mg MQMAS, Forsterite

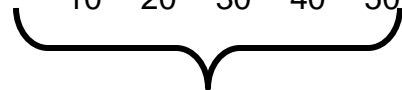
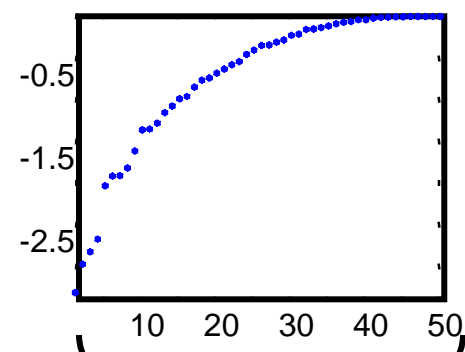
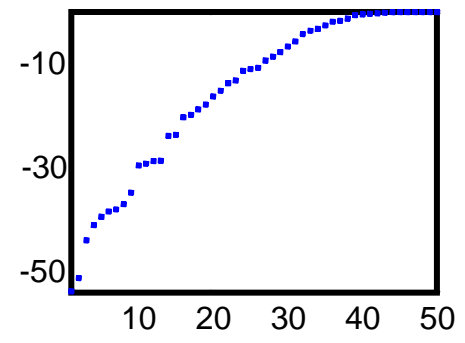
Isotropic
projection



spectrum



$a^T \cdot a$



$$\lambda_j = \frac{I_j \cdot \text{eig}(a^T \cdot a)}{\sum_{j=1}^N I_j}$$

Support Vector Machines

- Machine Learning for overlapping decision regions traditionally used back propagation ANN.
- Last decade SVM has proven popular owing to computational tractability; given set G of input $\{x_i\}$ output $\{a_i\}$ data, non-linear functions ψ_i map input data to higher dim feature space.
- SVM regression function has weights w_i and constants b , adjusted via *regularized risk minimization*:

$$f = g(x) = w_i \psi_i(x) + b$$

- *Using features extracted from NMR spectra $\{a_i\}$ in conjunction with structural details $\{x_i\}$ one may perform structure prediction...*

Ensemble SVM

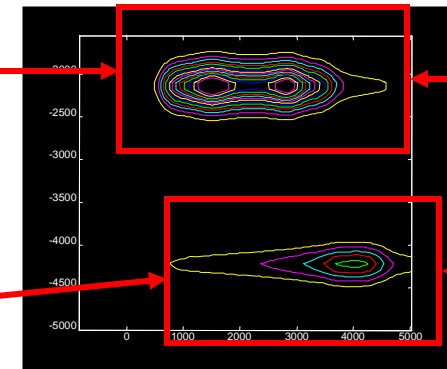
- Assign a single SVM to each atomic position component eg., for Forsterite unit cell, 6atoms x 3 (xyz) = 18 SVM's
- There are two distinct Mg sites in forsterite MQMAS spectra -> use ensemble of *two* SVM grids, weighted by training accuracy
- *Input:* (each grid element) 50 eigenvalues
- *Output:* (each grid element) one atomic position component

Atomic Positions

Si_x	Si_y	Si_z
$1Mg_x$	$1Mg_y$	$1Mg_z$
$2Mg_x$	$2Mg_y$	$2Mg_z$
$1O_x$	$1O_y$	$1O_z$
$2O_x$	$2O_y$	$2O_z$
$3O_x$	$3O_y$	$3O_z$

$$\begin{array}{cccc}
 & SVM_{2,1} & \cdots & SVM_{2,3} \\
 SVM_{1,1} & \cdots & \vdots & SVM_{1,3} \\
 \vdots & SVM_{2,16} & \cdots & SVM_{2,18} \\
 SVM_{1,16} & \cdots & SVM_{1,18} &
 \end{array}$$

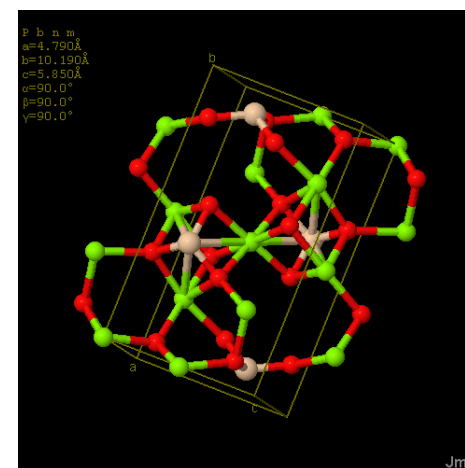
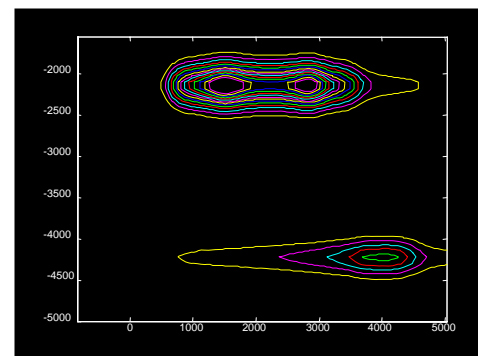
Ensemble SVM



^{25}Mg MQMAS

Results

- 50 sets of input structures produced with random displacements of $< 5\%$
- *Ab initio* performed in ESPRESSO, custom software used to simulate MQMAS spectra using calculated C_q and η
- SVMlight is used for ensemble creation/training, using $2*50*50$ features, matched with atomic coordinate components
- *Ensemble processing MQMAS spectra produced from trial structures reproduce structure to within 10%*
- Accuracy should increase further with larger training set, more accurate ab initio (these abbreviated runs ~ 20 mins each on dual Xeon)



Current Work

- Procedure as outlined works for when some insight exists as to structure eg., useful for understanding structural phase changes
- A large amount of work is devoted to understanding uptake of heavy elements in minerals
- Ideally would like to extend this method to predicting substitution sites and percentage uptakes of Cs,Sr in (for example) zeolites, clays etc
- Application to disordered materials eg., glasses, solid solutions
- Surface science eg., studies of liquid/solid interface etc

Conclusions

- Solid State NMR is powerful local probe of atomic structure, impeded by need for simulation, ab initio and/or empirical calculations
- Collaboratories provide wealth of information in the form of experimental, calculated and document data such as figures, tables etc
- Machine Learning techniques eg., SVM may be trained on said data using features described herein, to give direct insight into local atomic structure.
- Methods outlined have promising applications besides structural morphology eg., sequestration

Acknowledgements

- Microsoft
- National Science Foundation

References

- T. Joachims, **Making large-Scale SVM Learning Practical**. Advances in Kernel Methods - Support Vector Learning, B. Schölkopf and C. Burges and A. Smola (ed.), MIT-Press, 1999.
- **ESPRESSO** <http://www.quantum-espresso.org/>
- Brouwer, W. J; Davis, M. C.; Mueller, K. T., **Optimized Multiple Quantum MAS Lineshape Simulations in Solid State NMR** *Computer Physics Communications* (Submitted).