Anharmonicity, electron-lattice coupling, and superconductivity in hydrogen-rich systems

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Outline

Metallization of Hydrogen

Prediction: Metallic state

E. Wigner i H. B. Huntington, J. Chem. Phys. **3**, 764 (1935):

- $H - H$ distance (d_{HH}),
- Wigner-Seitz radius ($r_s \equiv (\frac{3}{4\pi n})^{1/3}$).

Metallization at $p \approx 25 GPa$: $2r_s > d_{HH}$.

Prediction: Superconductivity in $300K$

N. Ashcroft, PRL **21**, 1748 (1968)
$T_C = \Theta_D \mathcal{F}(\text{el.-ph.})$

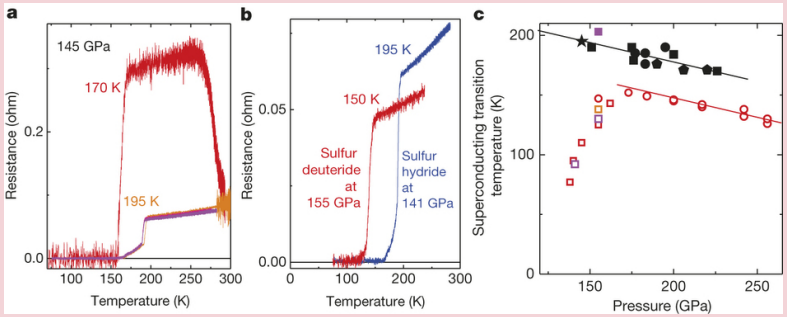
	T_C (K)
Jupiter surface	$\sim 10^{-27}$
Jupiter core	~ 290

Experiment: Metallicity (2017)

R. P. Dias, I. F. Silvera, Science 10.1126/science.aal1579
M. I. Eremets, P. P. Kong, A. P. Drozdov, arXiv:2109.11104 (2021)

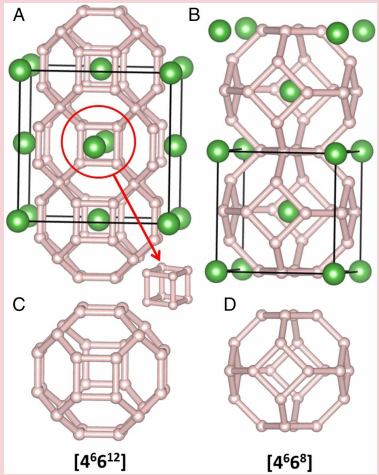
Experiment: Superconductivity

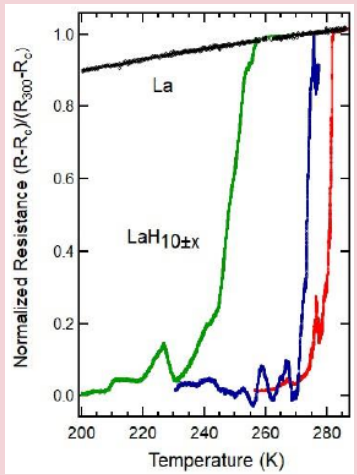
$H_{2|3}S$



A. P. Drozdov et al., Nature **525**, 73 (2015)

$LaH_{10 \pm x}$



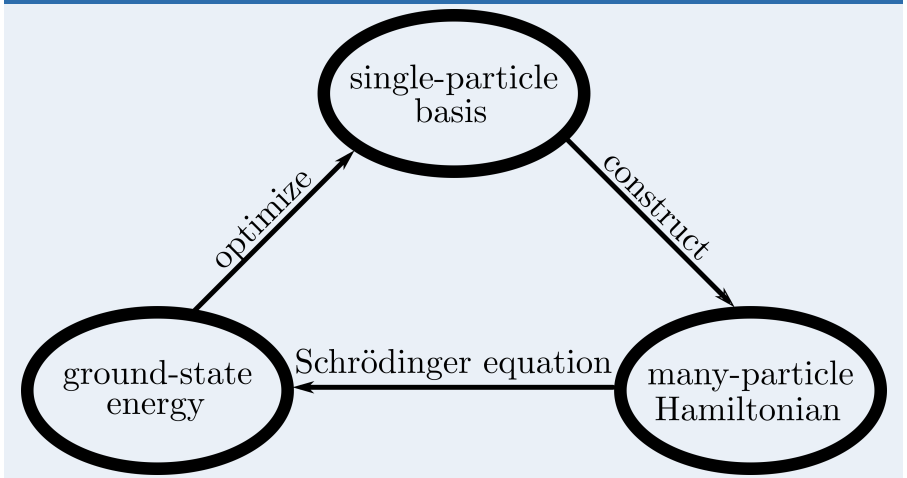


$L_{th.}$: Hanyu Liu et al., PNAS 114, 27 (2017)

$R_{exp.}$: M. Somayazulu et al., arXiv:1808.07695 (2018)

Exact Diagonalization Ab Initio (EDABI++)

Outline



♠ J. Spałek et al., Phys. Rev. B **61**, 15676 (2000);
♦ A. Biborski, APK, J. Spałek, Comput. Phys. Commun. **197**, 7 (2015);
♡ A. Biborski, APK, J. Spałek, Phys. Rev. B **98**, 085112 (2018).

Conservation of complexity

Switching to the second quantization is effective only for the orthogonal bases (otherwise $\left\{\hat{c}_i, \hat{c}_j^\dagger\right\} = \mathbb{S}_{ij}$ or $\hat{c}^{\dagger i} \equiv \mathbb{S}^{ij}\hat{c}_j^\dagger$).

LCAO

Orthogonal basis $\{w_i\}$ a linear combination of STO $\{\psi_i\}$:
$w_i(\mathbf{r}) \equiv \sum_k \beta_j \psi_j(\mathbf{r})$,
$\langle w_i | w_j \rangle = \delta_{ij}$.

With a mixing matrix $\mathbb{W}_{ij} \equiv \langle w_i | \psi_j \rangle$.

- Löwdin orthogonalization
  - ♪ solution close to starting orbitals
  - ∅ dense $\mathbb{W}$
  - ∅ requires sharp cut-off for infinite systems
- quadratic forms
  - ∅ many solutions
  - ♪∅ symmetry constrains
  - ♪ sparse $\mathbb{W}$
  - ♪ systematic approach to infinity

Hamiltonian

Hamiltonian and its parameters

We work with the second-quantization Hamiltonian

$$\mathcal{H} = \sum_{i\sigma} \epsilon_i \hat{n}_{i\sigma} + \sum_{i\neq j\sigma} t_{ij} \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma} + \sum_{i} U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i\neq j} K_{ij} \hat{n}_i \hat{n}_j$$
$$- \sum_{i\neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} \sum_{i\neq j} J_{ij} \hat{n}_i \hat{n}_j + \sum_{i\neq j} J_{ij} \hat{c}^{\dagger}_{i\uparrow} \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{j\downarrow} \hat{c}_{j\uparrow}$$

with fermionic creation/annihilation operators

$$\{\hat{c}^{\dagger}_{i\sigma}, \hat{c}^{\dagger}_{j\sigma'}\} \equiv \{\hat{c}_{i\sigma}, \hat{c}_{j\sigma'}\} \equiv 0 \quad \text{and} \quad \{\hat{c}^{\dagger}_{i\sigma}, \hat{c}_{j\sigma'}\} \equiv \delta_{ij}\delta_{\sigma\sigma'},$$

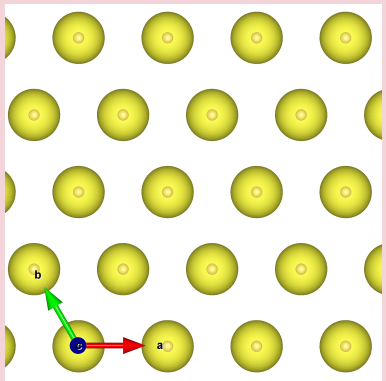
and the microscopic parameters

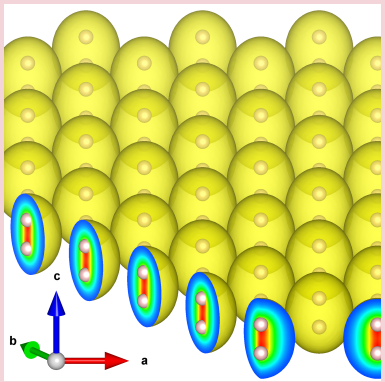
$$t_{ij} = \left\langle w(\mathbf{r})_i \middle| -\nabla^2 - \sum_{k=1}^{n} \frac{2}{|\mathbf{r} - \mathbf{R_k}|} \middle| w(\mathbf{r})_j \right\rangle, \qquad \epsilon_i \equiv t_{ii}$$

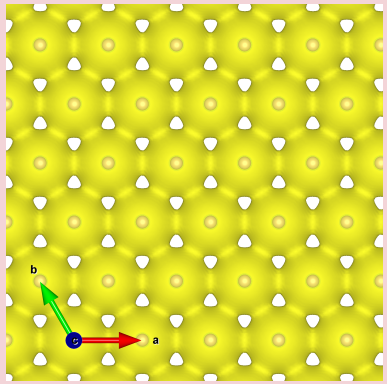
$$V_{ijkl} = \left\langle w(\mathbf{r})_i w(\mathbf{r}')_j \middle| \frac{2}{|\mathbf{r} - \mathbf{r}'|} \middle| w(\mathbf{r}')_k w(\mathbf{r})_l \right\rangle. \qquad U \equiv V_{iiii},\ K_{ij} \equiv V_{ijji},\ J_{ij} \equiv V_{ijij},$$

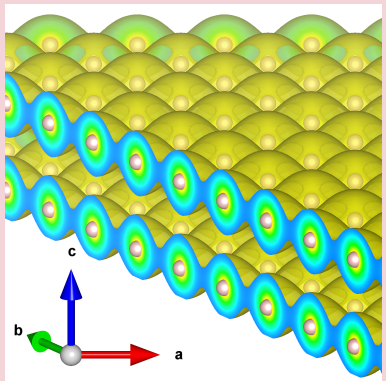
Triangular lattice

Two-dimensional crystal



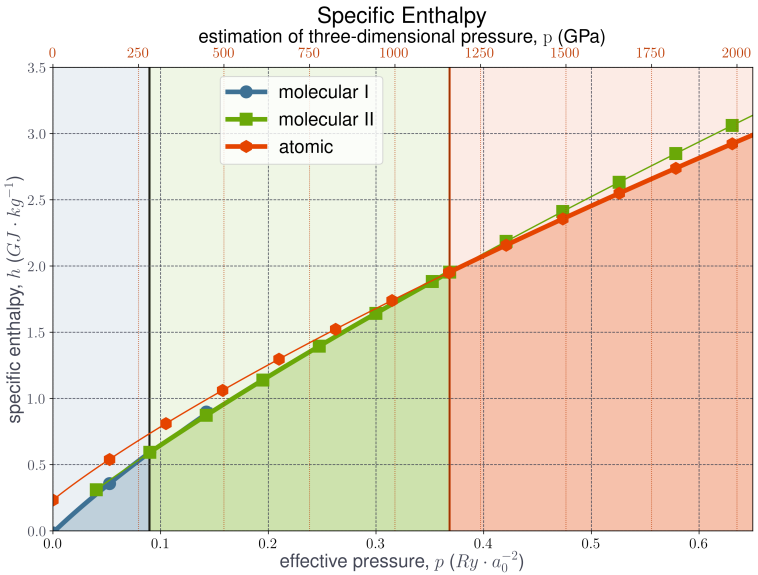


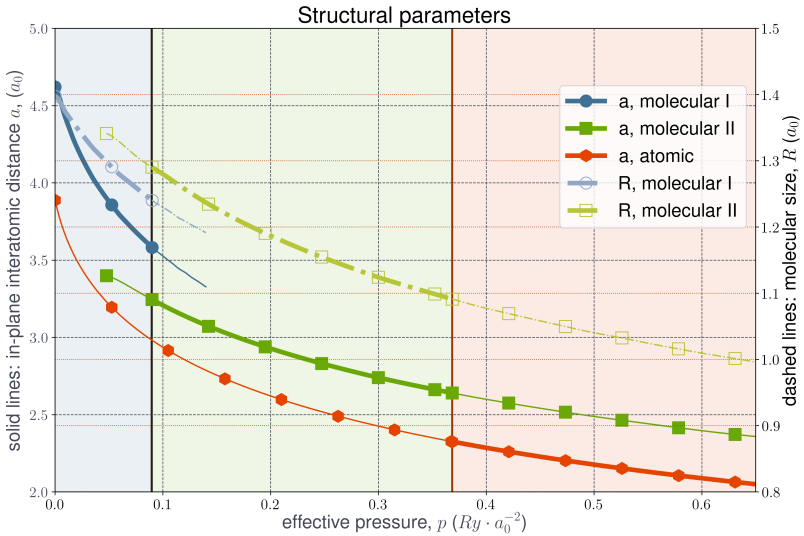




- periodic boundary conditions in xy plane;
- Lanczos algorithm for the diagonalization core of 6 and 8 atoms ;
- wavefunction constructed from 10 classes of nodes
  - ↪ hoppings t_{ij} up to 10^{th} neighbor;
  - ↪ Coulomb repulsion K_{ij} up to 10^{th} neighbor;
  - ↪ ferromagnetic exchange J_{ij} up to 3^{rd} neighbor;

2D enthalpy and lattice parameters



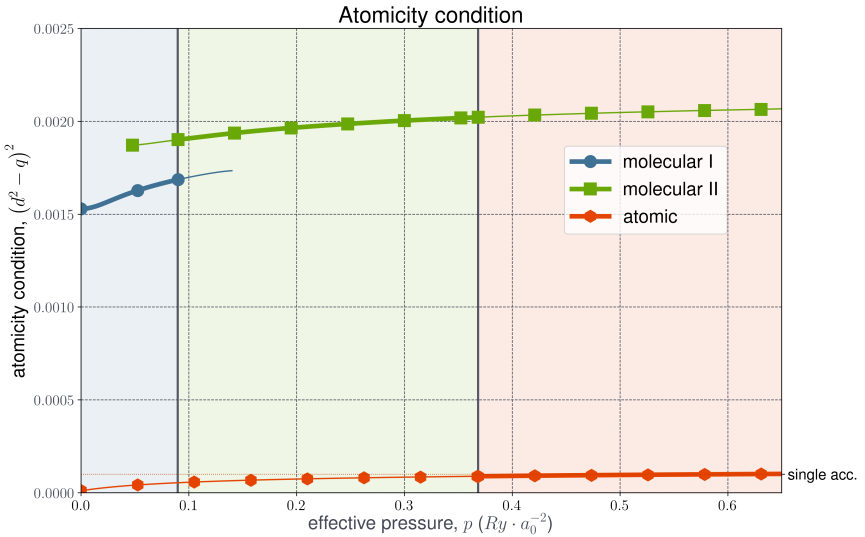


Question:

What is the quantum equivalent of $R_{eff} \to \infty$?

$$\delta d \equiv \left(P \begin{pmatrix} * \\ \uparrow\downarrow \end{pmatrix} P \begin{pmatrix} \uparrow\downarrow \\ * \end{pmatrix} - P \begin{pmatrix} \uparrow\downarrow \\ \uparrow\downarrow \end{pmatrix} \right)^2$$

$$\equiv \left(\langle \Phi_0 | \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} | \Phi_0 \rangle \langle \Phi_0 | \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} | \Phi_0 \rangle - \langle \Phi_0 | \hat{n}_{1\uparrow} \hat{n}_{1\downarrow} \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} | \Phi_0 \rangle \right)^2$$



Magnetic order

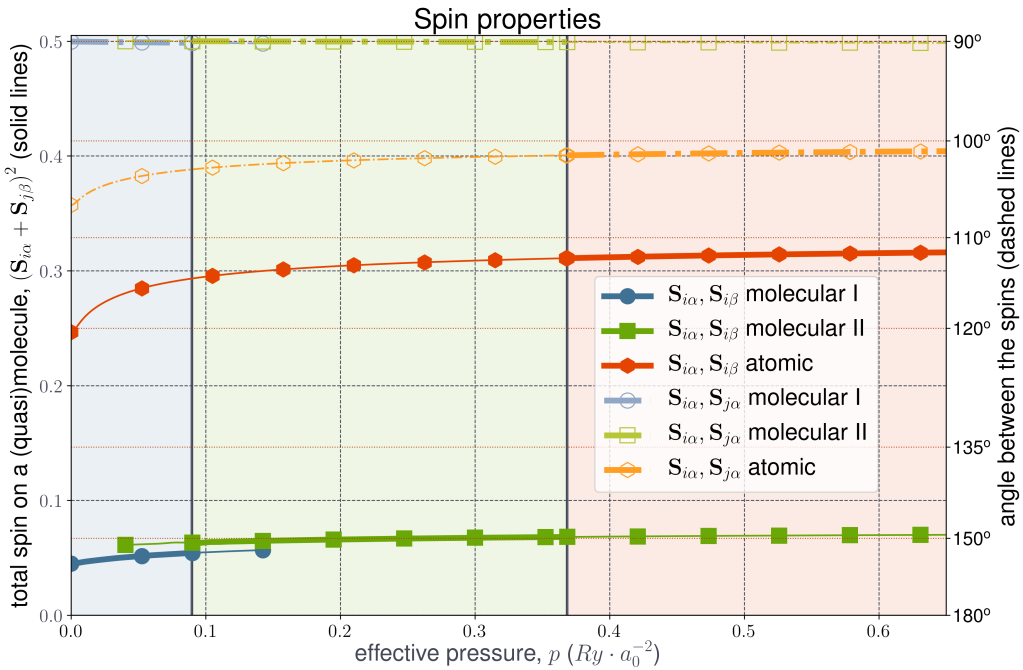
FM vs. AFM exchange

$J_{\text{FM, Hund-like}} \ll J_{\text{AFM, kinetic}}$

Required for the ambient pressure stability of the atomic phase!

Spin correlation

1. Molecular phases: molecular near spin-singlet H_2
2. Atomic phase: near 120° Néel order



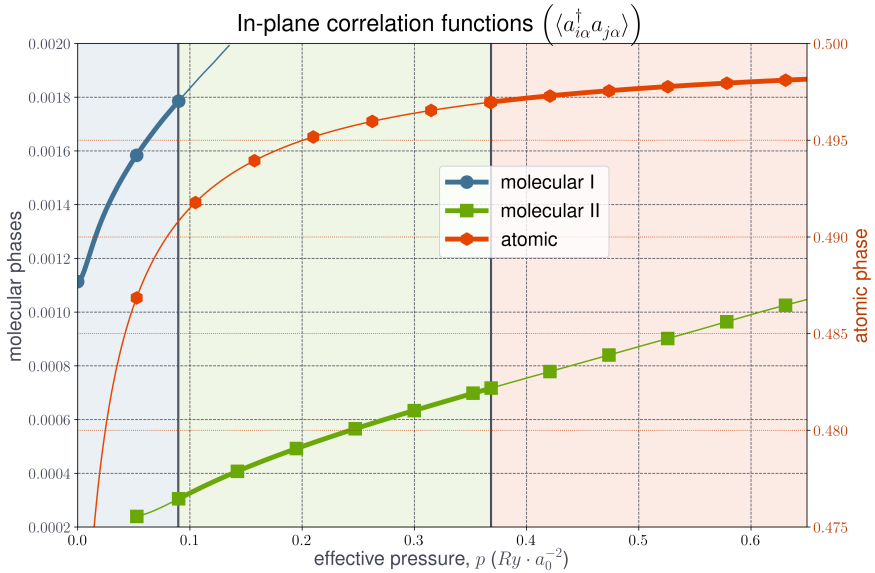
Total spin

	mol. I → II		mol. II → atomic	
$\|\|\mathbf{S}\|\|_{\text{molecule}}$	0.10	0.14	0.16	0.54
$\|\|\mathbf{S}\|\|_{\text{triangle}}$	0.86	0.87	0.86	0.077

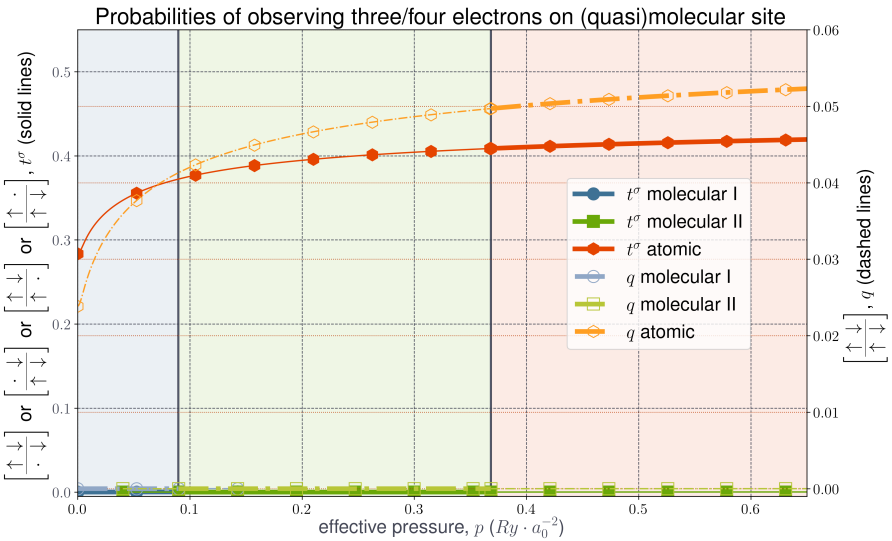
$$||\mathbf{S}||_{\mathbf{molecule}} \equiv ||\mathbf{S}(\mathbf{x}_{2D}, -\tfrac{R}{2}) + \mathbf{S}_2(\mathbf{x}_{2D}, \tfrac{R}{2})||$$

$$||\mathbf{S}||_{\mathbf{triangle}} \equiv ||\mathbf{S}(\mathbf{x}_{2D}, \tfrac{R}{2}) + \mathbf{S}(\mathbf{x}_{2D} + \mathbf{e_1}, \tfrac{R}{2}) + \mathbf{S}(\mathbf{x}_{2D} + \mathbf{e_2}, \tfrac{R}{2})||$$

Metallization I: Correlation Functions



$$\mathcal{C}_{ij} \equiv \left\langle \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma} \right\rangle = \left\langle \Phi_0 \middle| \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma} \middle| \Phi_0 \right\rangle_G$$

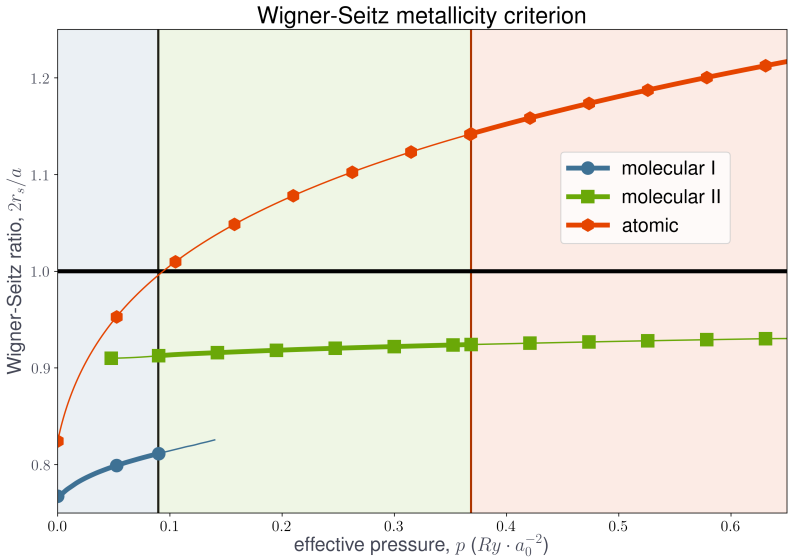


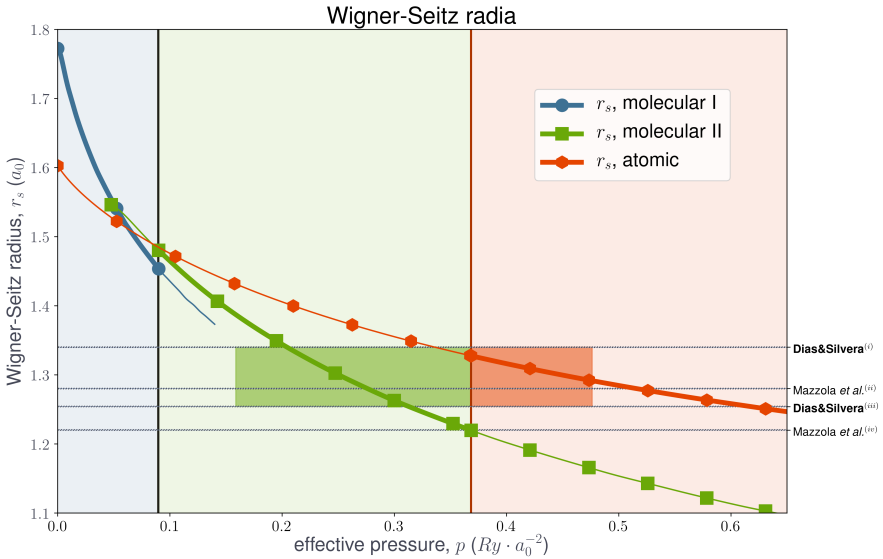
$$q \equiv P\left(\begin{array}{c}\uparrow\downarrow\\ \uparrow\downarrow\end{array}\right) \qquad d_0 \equiv P\left(\begin{array}{cc}\uparrow & \\ & \downarrow\end{array}\right)$$

$$t_{\uparrow} \equiv P\left(\begin{array}{c}\uparrow\\ \uparrow\downarrow\end{array}\right) \qquad d_{\uparrow} \equiv P\left(\begin{array}{c}\uparrow\\ \uparrow\end{array}\right)$$

$$t_{\downarrow} \equiv P\left(\begin{array}{c}\downarrow\\ \uparrow\downarrow\end{array}\right) \qquad d_{\downarrow} \equiv P\left(\begin{array}{c}\downarrow\\ \downarrow\end{array}\right)$$

Metallization II: Wigner-Seitz Criterion





$$r_S \equiv \left(\frac{3}{4\pi n}\right)^{1/3}$$

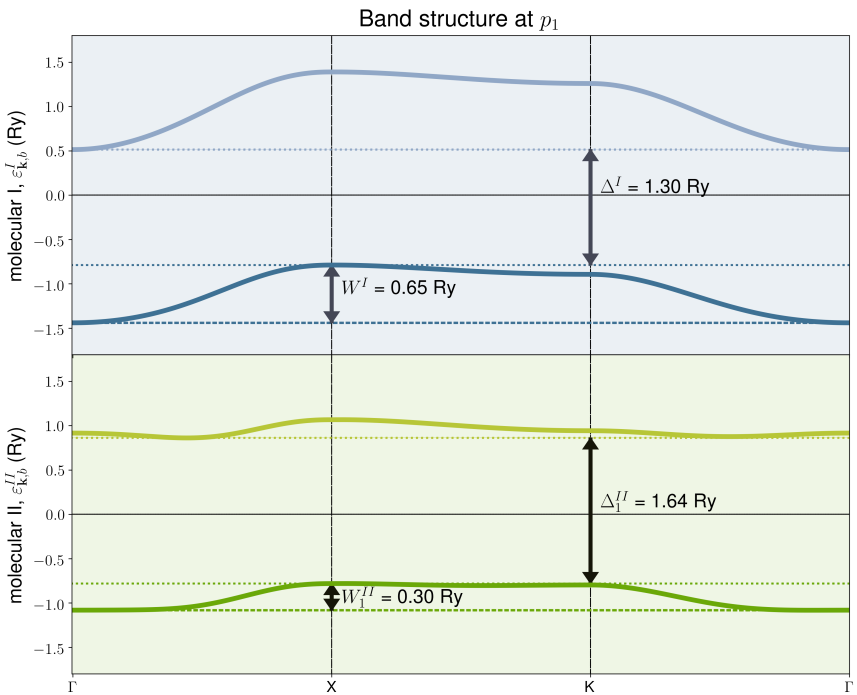
$$\text{metal} \Leftrightarrow 2r_s > d_{HH}$$

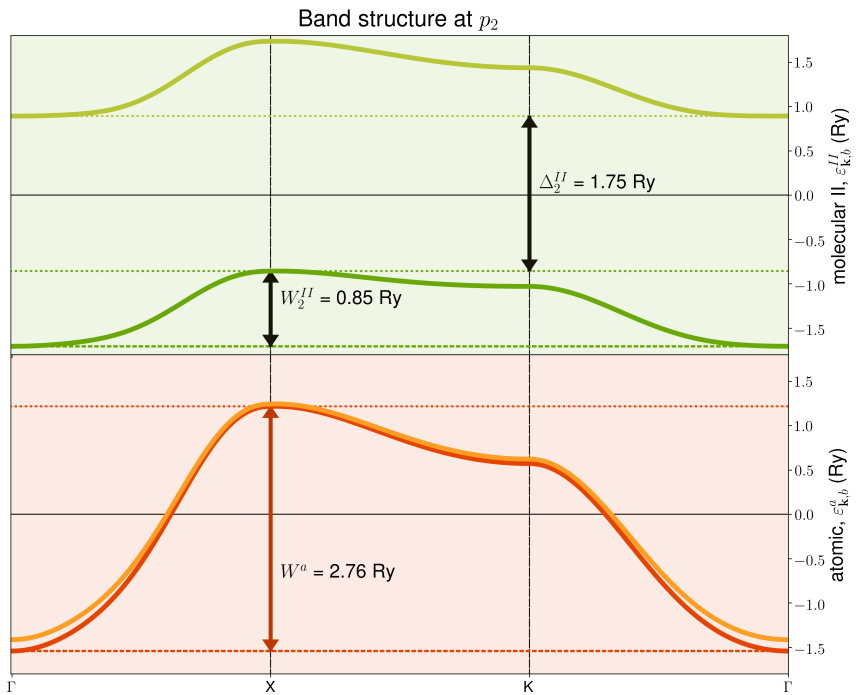
Can be found experimentally!

source	method	$r_s(a_0)$
Min et al., PRB **33**, 324 (1986)	LMTO	2.85
Pfrommer et al., PRB **58**, 12680 (1998)	GGA-PW91	2.50
Svane et al., SSC **76**, 851 (1990)	LSDA	2.45
Li et al. PRB **66**, 035102 (2002)	LSDA	2.78
Li et al. PRB **66**, 035102 (2002)	PBE	2.50
Mazzola et al., Nat.C. **5**, 3487 (2014)$^{(i)}$	DMC + MD	**1.28**$^{(ii)}$
McMinis et al., arXiv:1309.7051 (2013)	DMC	2.27
AB,APK,JS, PRB **96**, 085101 (2017)$^{(iii)}$	EDABI	**1.27**
molecular II	EDABI	$\mathbf{1.22}^{+0.17}_{-0.06}$
atomic	EDABI	$\mathbf{1.33}^{+0.10}_{-0.04}$
Dias & Silvera	experiment	**1.297(43)**

Metallization III: Band structure

Bare bands	Correlated bands	Bands + Correlator
■ easily calculable	■ full $\mathcal{H}$ dependence	■ calculable
■ depend only on $\mathcal{H}_{\text{free}}$	■ no generic method	∅ correlator physics





Possibility of superconducting state

Bypassing **Eliashberg theorem**

$$T_C = T_C(\Theta_D, \lambda, \mu^*)$$

- Θ_D - Debye T (from phonon DOS)
- λ - electron–phonon coupling (from phononic and electronic dispersion)
- μ^* - Morel-Anderson pseudopotential - from absolute energy scale

Morel-Anderson pseudopotential

$$\mu^* = \frac{\mu}{1 + \mu \log(\frac{\mathrm{T}_{\mathbf{phonons}}}{\mathrm{T}_{\mathbf{electrons}}})}$$

$$\mu^* = \frac{n(E_F)(U - K_1)}{1 + n(E_F)(U - K_1) \log(\frac{E_f}{k_B \Theta_D})}$$

Electron - phonon coupling

Eliashberg spectral function

$$\alpha^2 F_{\mathbf{k}}(\omega) \approx \sum_\nu \int d\mathbf{q} g_\nu^{\mathbf{k}\mathbf{k}'} \delta(\omega - \omega_\eta) \delta(\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}+\mathbf{q}))$$

allows us to obtain electron-phonon coupling constant

$$\lambda = 2 \int_{\mathbf{0}}^{\infty} \frac{d\omega}{\omega} \alpha^2 F_{\mathbf{k_f}}(\omega)$$

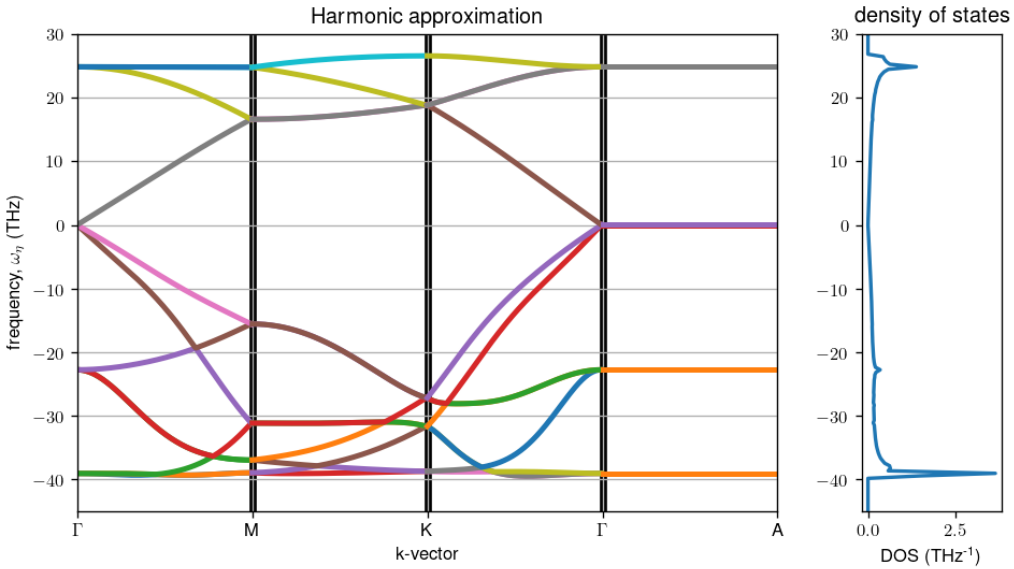
Spectral function

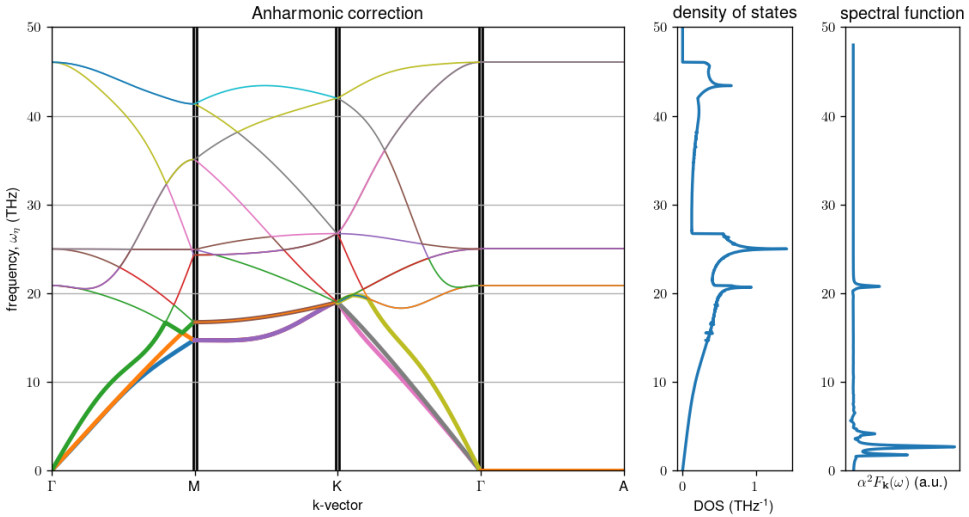
$$t_{ij} \to t_{ij} + \delta t_{ij} = t_{ij} + \sum_\nu \frac{\delta t_{ij}}{\delta \mathbf{u}_\nu} \delta \mathbf{u}_\nu$$

$$\sum_{ij} \delta t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} \to \text{Fourier Transform}$$

$$\overset{\text{DFT}}{\equiv} \sum_{\mathbf{k},\mathbf{k}',\nu} g_\nu^{\mathbf{k}\mathbf{k}'} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{\mathbf{k}'\sigma} (b_\nu^\dagger + b_\nu)$$

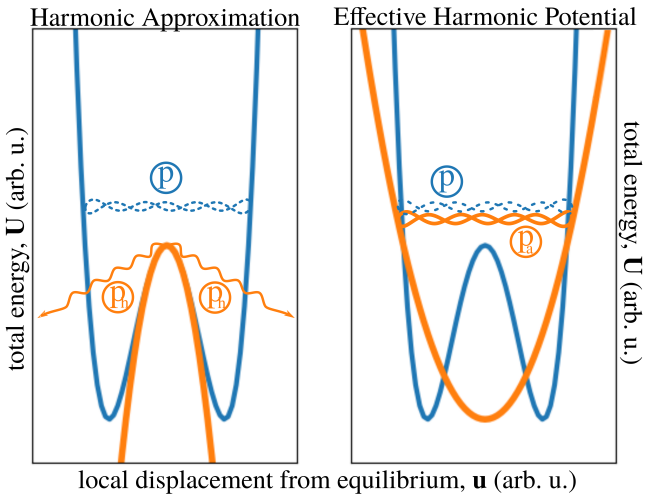
Electrons and Phonons: DFT calculations with EDABI constrains





We take the Mexican-hat potential:

$$U(\{u^i\}) = U_0 + \frac{1}{2}\Phi_{ij}u^{ij} + \frac{1}{4!}\Phi_{ijkl}u^{ijkl}$$



$$\mathbf{F}_i \to \mathbf{F}_i + \frac{1}{4!}\Phi_{i;j\langle kl\rangle}u^{ij\langle kl\rangle}.$$

At $p_{\text{eff}} = 0.7Rya_0^{-2}$ $(\sim 1TPa)$

$U_{\text{eff}} \equiv U - K_{pl}$ (Ry)	μ^*	λ
1.194	0.192	1.05
Θ_D (K)	T_C (K)	T_{AD} (K)
1300	164	**176**

DFT (VASP): SCAN meta-GGA + vdW corrections + charge from EDABI

Conclusions 2D

Physics of hydrogen planes

- concomitant atomization & metallization;
- long-range interactions ($\sim ||\mathbf{R}||^{-p}$);
- London-like interactions in insulating molecular phases (true molecular crystal);
- weak London-like attraction of atomic planes;
- benchmark for infinite-system quantum chemistry (EDABI + QMT Quantum Metallization Tools);

Hydrogen-induced superconductivity

- **medianly** correlated system;
- anharmonic correction to force constants necessary;
- superconductivity induced by electron-phonon coupling;
- Morel-Anderson pseudopotential **from First Principles**;
- high critical temperature $T_C = 176K$;
- extreme pressure (chemical?);

Thank you for your attention