Atomic and cluster physics for warm dense matter

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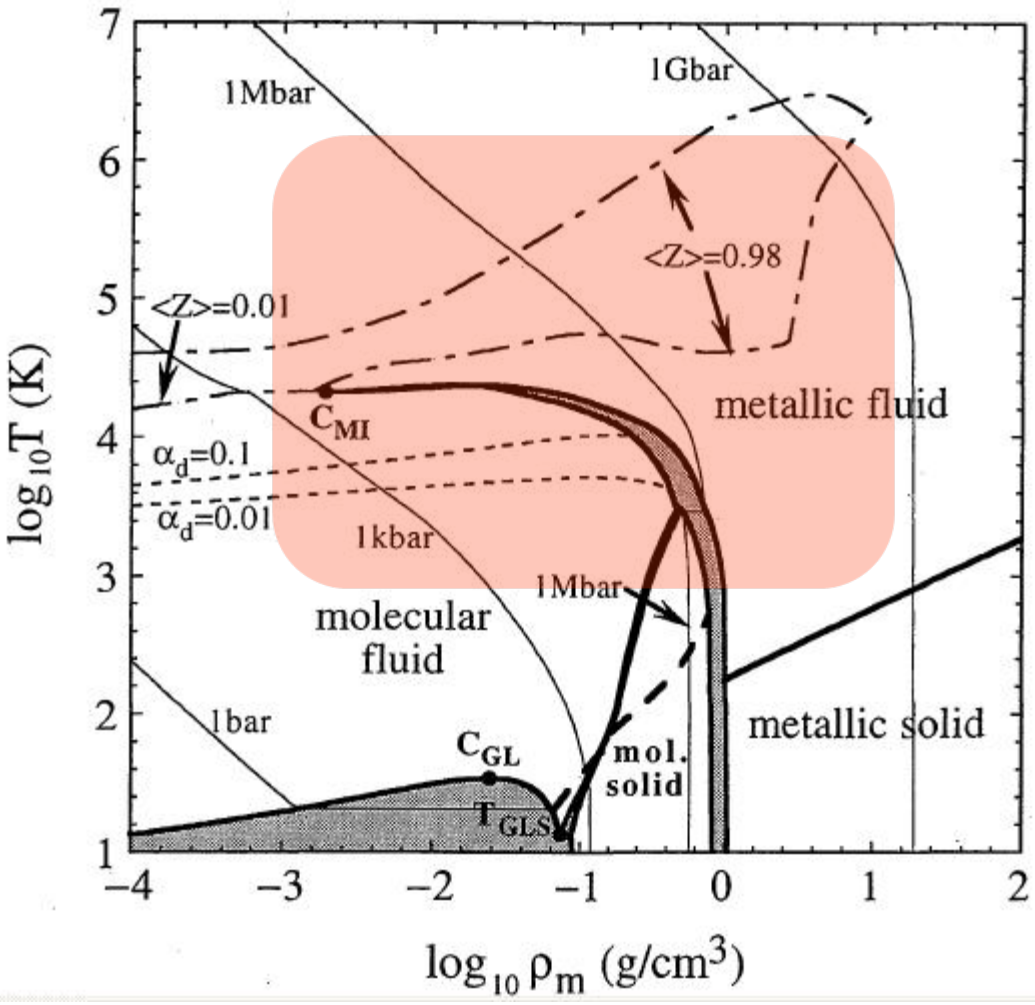
OUTLINE

1. Introduction to warm dense matter (WDM)
2. Quantum chemistry of clusters
3. Equation of state for mercury
4. *Ab initio* molecular dynamics
5. Photoexcitation kinetics of solids

1. Introduction to warm dense matter (WDM)

Phase diagram of hydrogen (theory)



WDM region

$n = 10^{20\text{-}24}$ cm^{-3}

$T = 10^{3\text{-}6}$ K

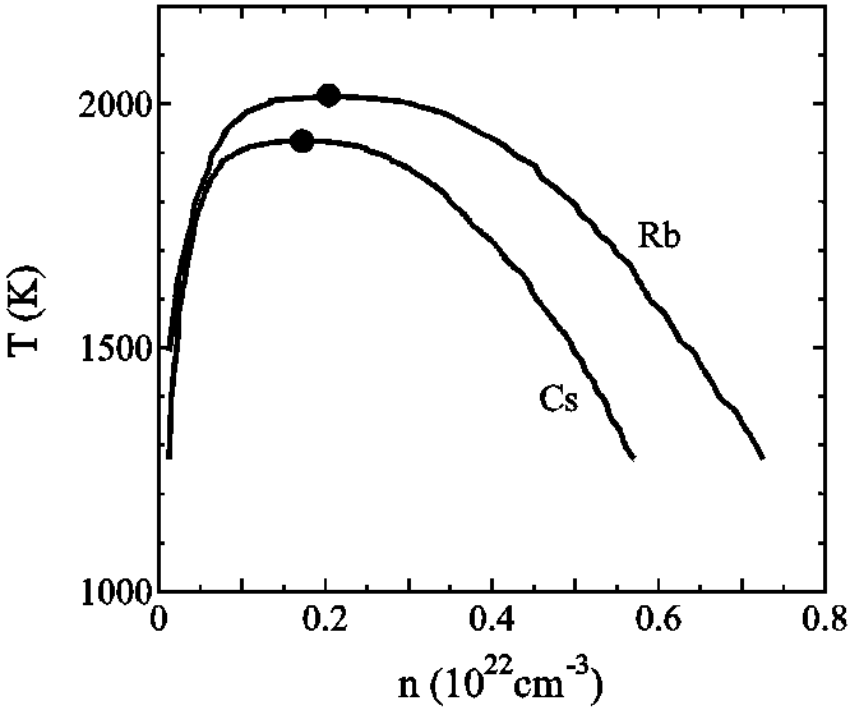
- metal-nonmetal transition
- molecular dissociation
- molecular liquid-solid transition

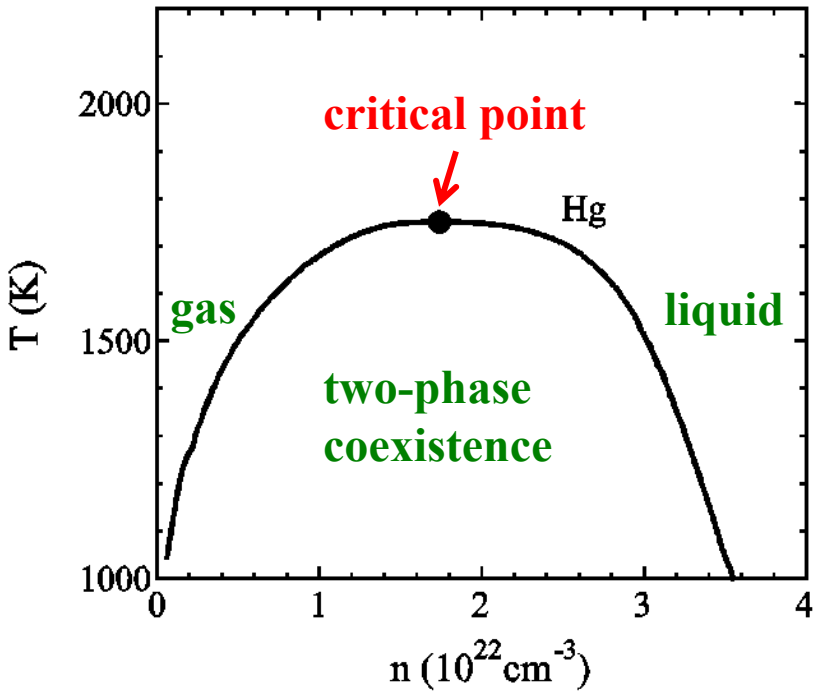
H.K. & S. Ichimaru,
J. Phys. Soc. Jpn **67**, 950 (1998)

Expanded fluid metals

F. Hensel & W.W. Warren, Jr.,
Fluid Metals (Princeton, 1999)

Gas-liquid coexistence curves (experimental)

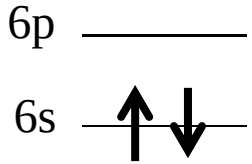




$_{37}$Rb(5s $^2S_{1/2}$)

$_{55}$Cs(6s $^2S_{1/2}$)

alkali metal



$_{80}$Hg(6s^2 $^1S_0$)

divalent metal

Critical points of fluid metals

Elements	T_c(K)	P_c(bar)	ρ_c(gcm^{-3})
Hg	**1751**	**1673**	**5.80**
Cs	1924	92.5	0.38
Rb	2017	124.5	0.29
K	2178	148	0.18
Na	2483	248	0.30
Li	3225	690	0.1
Al	8000	4470	0.64
Be	8100	11700	0.55
W, Sn, Au,..	?		

static experiments

dynamic experiments or extrapolation

large uncertainties

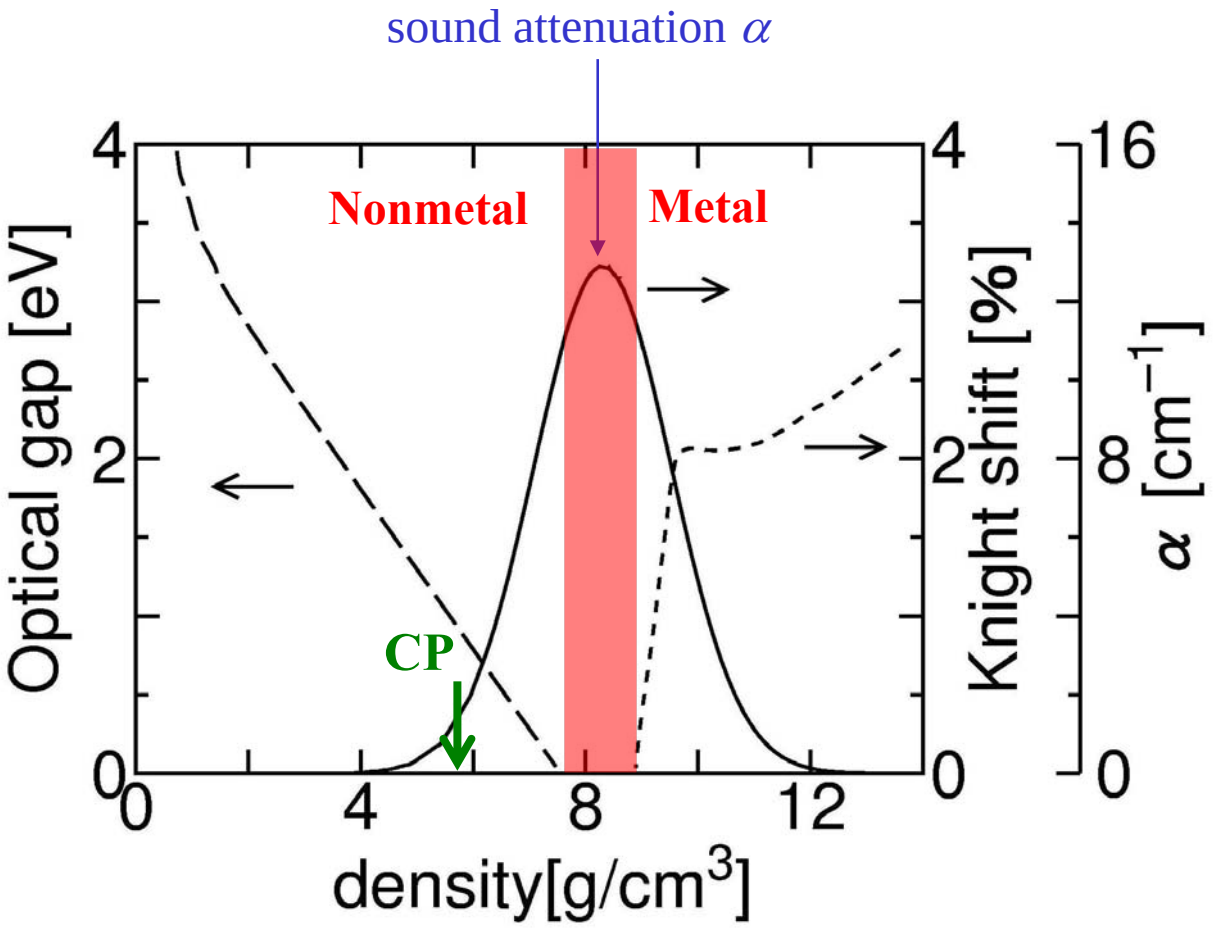
★ **Mercury has the lowest T_c → Prototypical element for WDM studies**

F. Hensel and W.W. Warren: *Fluid Metals* (Princeton, 1999)

V. Fortov, I. Iakubov & A. Khrapak: *Physics of Strongly Coupled Plasma* (Oxford, 2006)

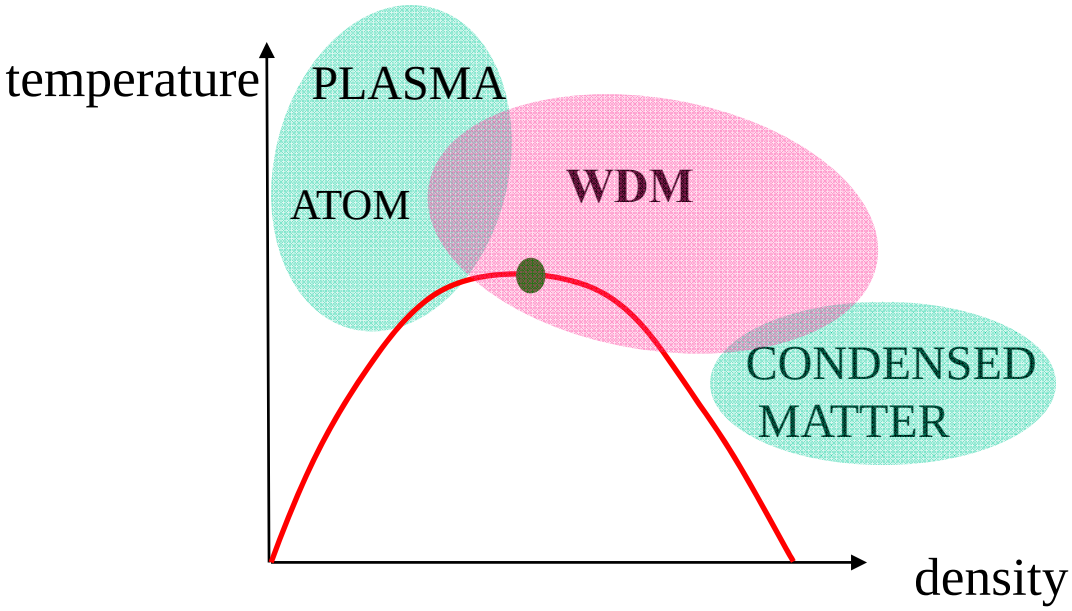
Metal-nonmetal transition in Hg at 9 g/cm^3

- Closure of 6s-6p gap
- Onset of Knight shift
- Anomalous sound absorption



Kohno & Yao, J. Phys.: Condens. Matter **13**, 10293 (2001)

M. Yao, Z. Phys. Chem. **185**, S73 (1994)



- Phase transitions among solid, liquid, gas, metallic and nonmetallic states occur in WDM region.

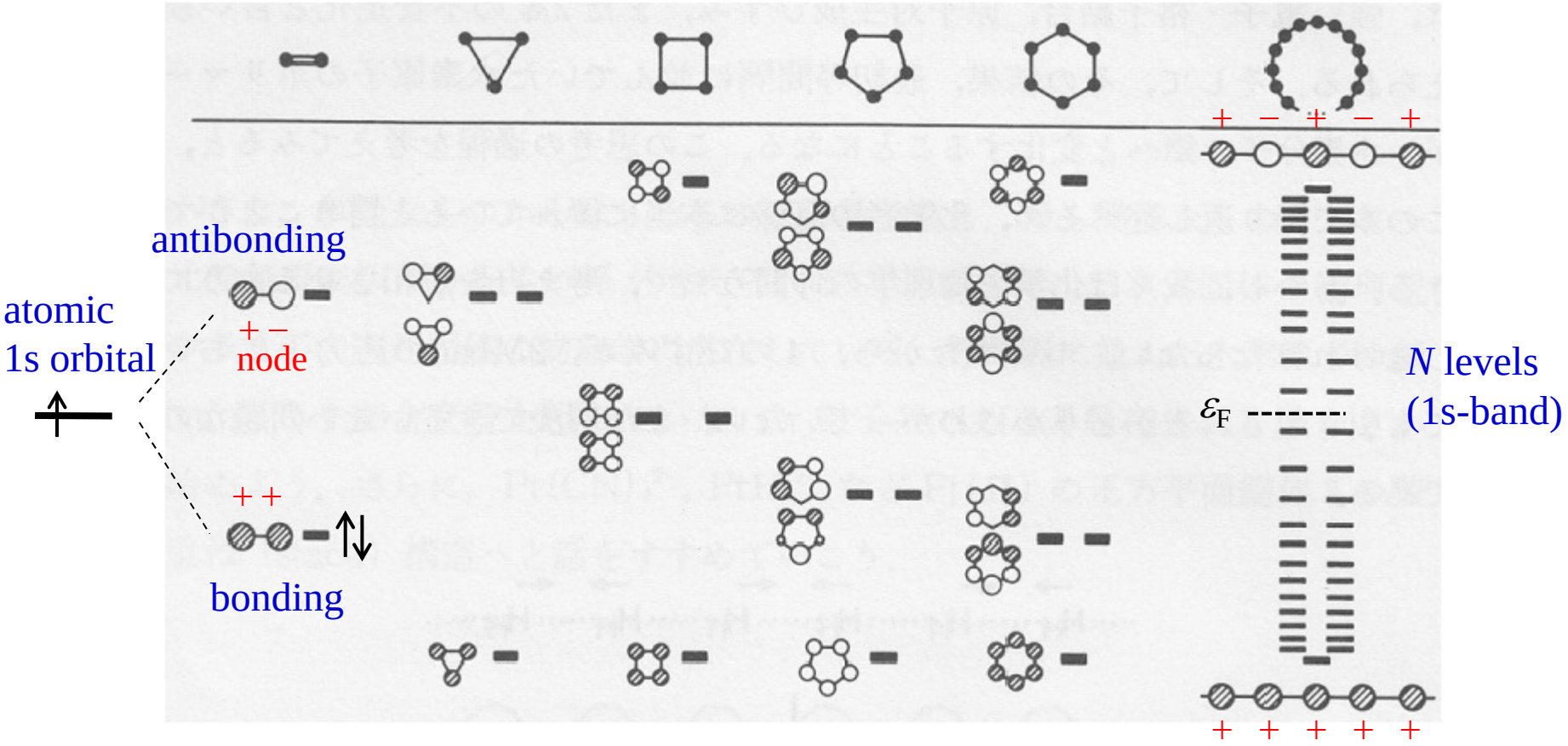
  → Importance of interatomic interactions

- Plasma, atomic, and condensed-matter concepts should be combined to predict WDM properties.

2. Quantum chemistry of clusters

Molecular orbitals (MOs) of hydrogen chains

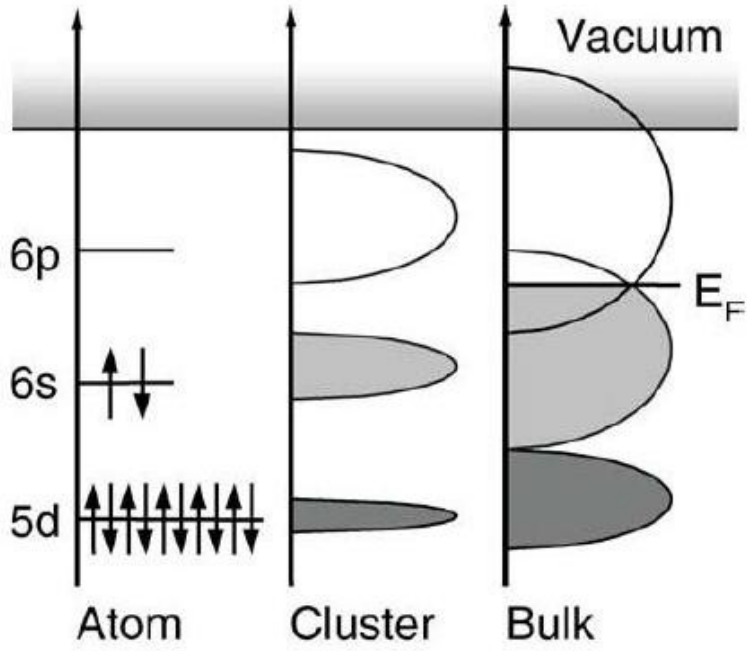
ONE-BAND SYSTEM



R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Systems* (VCH Publ., 1988), Sec. 2.

Metal-nonmetal transition in mercury clusters

TWO-BAND (6s,6p) SYSTEM



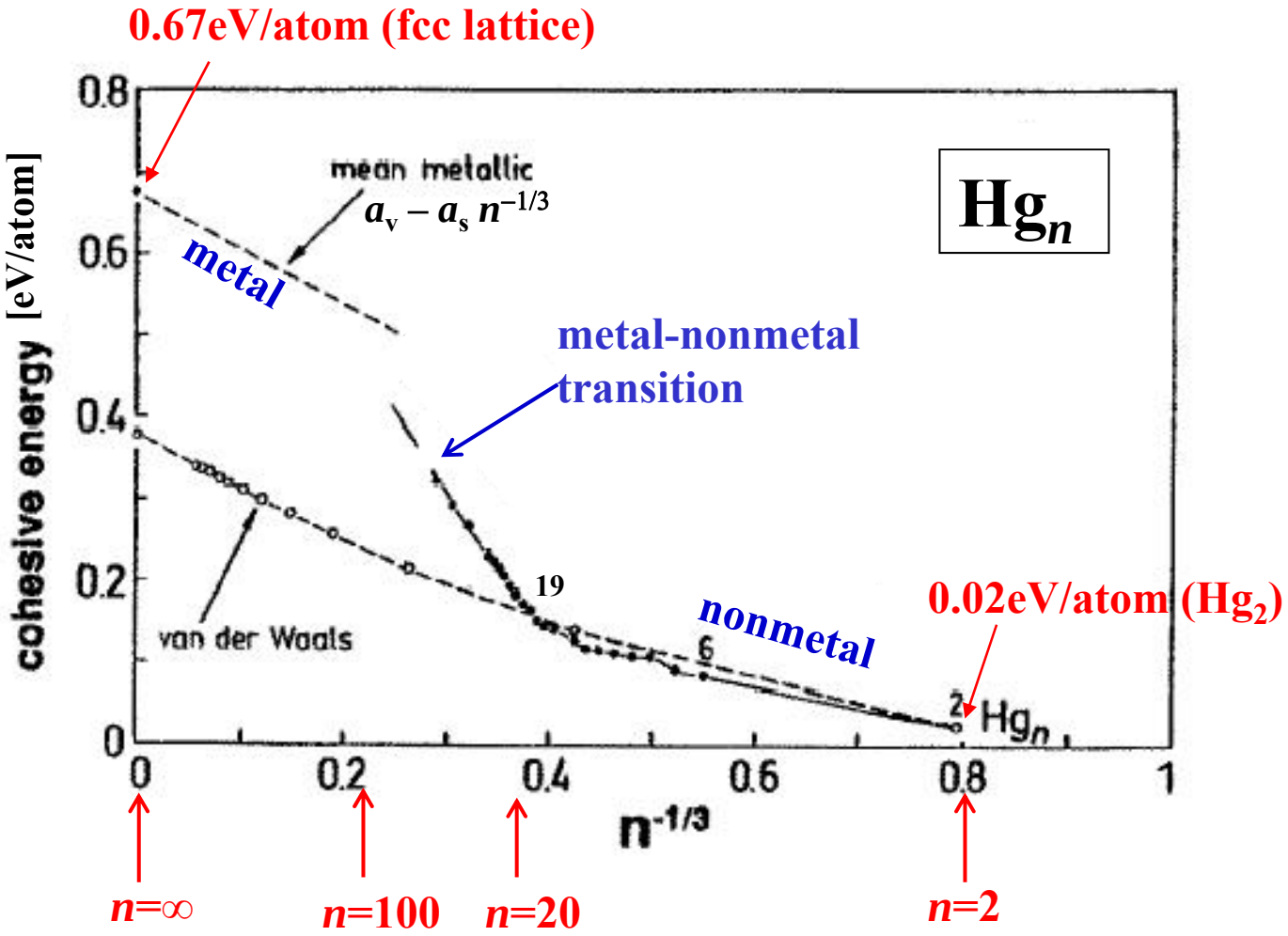
nonmetal

metal
(6s-6p overlap)

Hg_N cluster becomes a metal at $N = 400 \pm 30$ (photoemission spectroscopy)

B. von Issendorff & O. Cheshnovsky, Annu. Rev. Phys. Chem. **56**, 549 (2005)

M-NM transition enhances binding energies



Haberland, Kornmeier, Langosch, Oschwald & Tanner,
J. Chem. Soc. Faraday Trans. **86**, 2473 (1990)

Typical molecular-orbital (MO) method

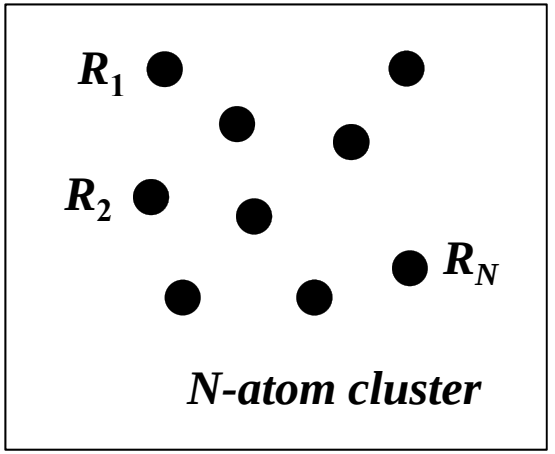
See e.g., Szabo & Ostlund, *Modern Quantum Chemistry* (Macmillan, 1982)

Step 1: LCAO-MO (linear combination of atomic orbitals)

$$\psi_k^{\sigma}(\mathbf{r}) = \sum_{\mu=1}^{N} \sum_{i=1}^{N_{\mathrm{STO}}} c_{k,i\mu}^{\sigma} \phi_i(\mathbf{r} - \mathbf{R}_\mu)$$

wave function of kth MO

$\sigma = \alpha, \beta$: spin



$$\phi_i(\mathbf{r}) = \left[\frac{(2\zeta_i)^{2n_i+1}}{(2n_i)!} \right]^{1/2} r^{n_i-1} \exp(-\zeta_i r) Y_{l_i m_i}(\theta, \varphi)$$

Slater-type atomic orbitals

quantum numbers (n_i, l_i, m_i)

i = 1s, 2s, 2p, etc.

Useful tables of ζ_i:

E. Clementi and C. Roetti, "Roothaan-Hartree-Fock Atomic Wavefunctions" At. Data Nucl. Data Tables **14**, 177 (1974)

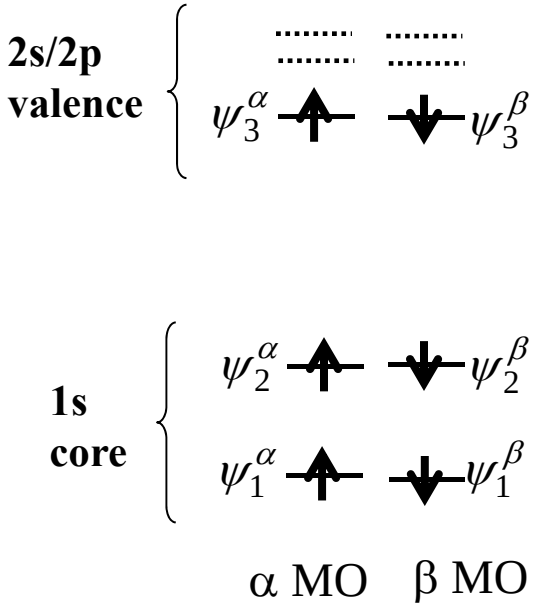
Note: In a solid, k = (band index + wave vector **k** within the Brillouin zone)

Step 2: Many-electron wavefunction

Unrestricted Hartree-Fock (UHF) approximation

$$\Psi(\mathbf{r}_1\sigma_1,\cdots,\mathbf{r}_{N_\mathrm{e}}\sigma_{N_\mathrm{e}}) = \frac{1}{\sqrt{N_\mathrm{e}!}}\sum_P (-1)^P P\Big[\psi^\alpha_{k_1}(\mathbf{r}_1)\alpha(\sigma_1)\cdots\psi^\alpha_{k_{N_\mathrm{e}^\alpha}}(\mathbf{r}_{N_\mathrm{e}^\alpha})\alpha(\sigma_{N_\mathrm{e}^\alpha}) \times\psi^\beta_{k_{N_\mathrm{e}^\alpha+1}}(\mathbf{r}_{N_\mathrm{e}^\alpha+1})\beta(\sigma_{N_\mathrm{e}^\alpha+1})\cdots\psi^\beta_{k_{N_\mathrm{e}}}(\mathbf{r}_{N_\mathrm{e}})\beta(\sigma_{N_\mathrm{e}})\Big]$$

Single Slater-determinant approximation applicable to open-shell systems



Example: Li_2 molecule

$N = 2$, $N_e = 6$

Step 3: Minimization of the total energy

$$H = \sum_{i=1}^{N_e}\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{\mu=1}^{N}\frac{-Z_\mu e^2}{\left|\mathbf{r}_i - \mathbf{R}_\mu\right|}\right] + \frac{1}{2}\sum_{\substack{i,j=1\\(i\neq j)}}^{N_e}\frac{e^2}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} + \frac{1}{2}\sum_{\substack{\mu,\nu=1\\(\mu\neq\nu)}}^{N}\frac{Z_\mu Z_\nu e^2}{\left|\mathbf{R}_\mu - \mathbf{R}_\nu\right|}$$

The total energy $E = \langle \Psi | H | \Psi \rangle$ is minimized under the subsidiary condition,

$$\int d\mathbf{r}\psi_{k_i}^{\sigma *}(\mathbf{r})\psi_{k_i}^{\sigma}(\mathbf{r}) = 1$$

$$\Rightarrow \quad \delta\left\{E - \sum_{i=1}^{N_e^\alpha}\varepsilon_i^\alpha \int d\mathbf{r}\psi_{k_i}^{\alpha *}(\mathbf{r})\psi_{k_i}^{\alpha}(\mathbf{r}) - \sum_{i=1}^{N_e^\beta}\varepsilon_i^\beta \int d\mathbf{r}\psi_{k_i}^{\beta *}(\mathbf{r})\psi_{k_i}^{\beta}(\mathbf{r})\right\} = 0$$

$$\Rightarrow \quad \sum_{\nu=1}^{N}\sum_{j=1}^{N_{\mathrm{STO}}}\left(F_{i\mu,j\nu}^{\sigma} - \varepsilon_k^\sigma S_{i\mu,j\nu}\right)c_{j\nu,k}^{\sigma} = 0 \qquad \sigma = \alpha, \beta$$

Step 4: Self-consistent solutions to MOs

$$\sum_{\nu=1}^{N}\sum_{j=1}^{N_{\mathrm{STO}}}\left(F^{\sigma}_{i\mu,j\nu}-\varepsilon^{\sigma}_{k}S_{i\mu,j\nu}\right)c^{\sigma}_{j\nu,k}=0 \qquad \text{for each } k,\ \sigma$$

Pople-Nesbet equation

J.A. Pople,
Nobel Prize in Chemistry, 1998

$$S_{i\mu,j\nu}\equiv\int d\mathbf{r}\,\phi_i^{*}(\mathbf{r}-\mathbf{R}_\mu)\phi_j(\mathbf{r}-\mathbf{R}_\nu) \qquad \text{overlap integral}$$

$$F^{\sigma}_{i\mu,j\nu}\equiv\int d\mathbf{r}\,\phi_i^{*}(\mathbf{r}-\mathbf{R}_\mu)H_{\mathrm{core}}(\mathbf{r})\phi_j(\mathbf{r}-\mathbf{R}_\nu) \quad\longleftarrow\quad H_{\mathrm{core}}(\mathbf{r})\equiv-\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla^2+\sum_{\mu=1}^{N}\frac{-Z_\mu e^2}{\left|\mathbf{r}-\mathbf{R}_\mu\right|}$$

$$+\sum_{\mu'=1}^{N}\sum_{i'=1}^{N_{\mathrm{STO}}}\sum_{\nu'=1}^{N}\sum_{j'=1}^{N_{\mathrm{STO}}}\left[\left(P^{\alpha}_{i'\mu',j'\nu'}+P^{\beta}_{i'\mu',j'\nu'}\right)\left(i\mu,j\nu\,|\,i'\mu',j'\nu'\right)-P^{\sigma}_{i'\mu',j'\nu'}\left(i\mu,j'\nu'\,|\,i'\mu',j\nu\right)\right]$$

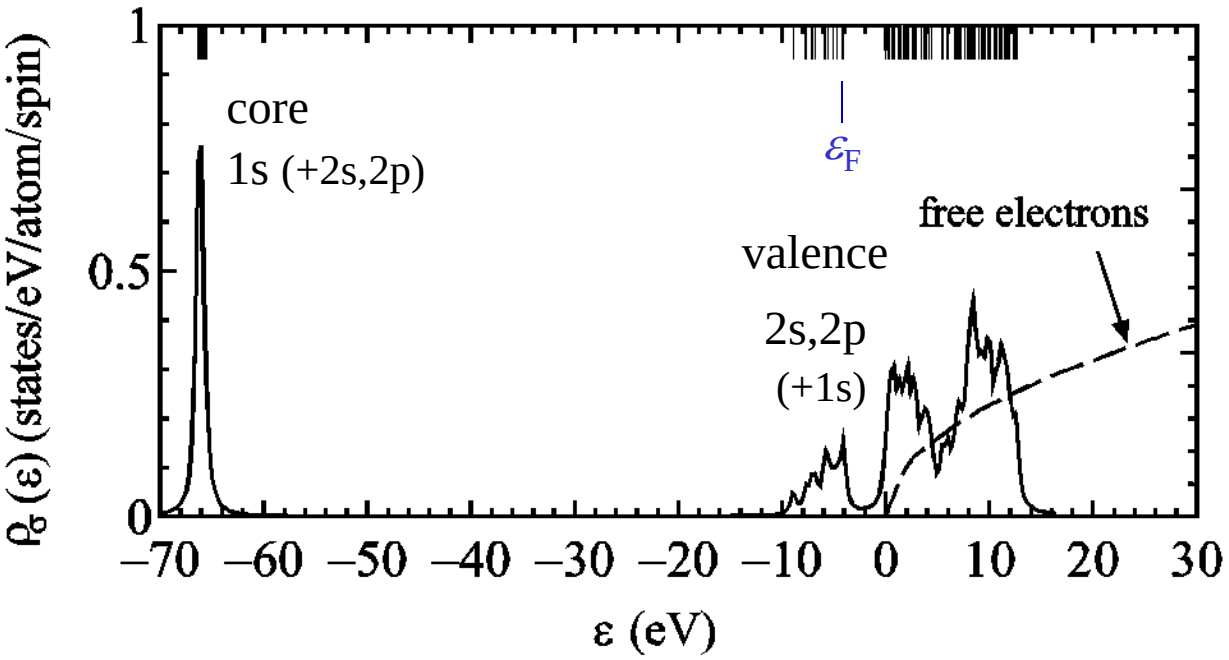
Fock matrix

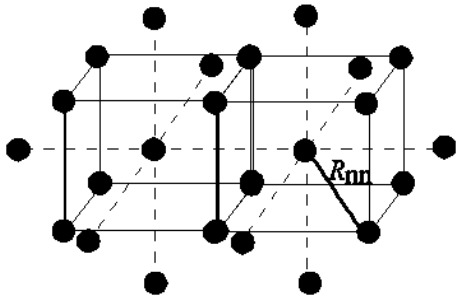
$$P^{\sigma}_{i\mu,j\nu}\equiv\sum_{k}^{occupied}c^{\sigma *}_{i\mu,k}c^{\sigma}_{j\nu,k} \qquad \text{bond-order matrix}$$

$$\left(i\mu,j\nu\,|\,i'\mu',j'\nu'\right)\equiv\int d\mathbf{r}_1\int d\mathbf{r}_2\phi_i^{*}\left(\mathbf{r}_1-\mathbf{R}_\mu\right)\phi_j\left(\mathbf{r}_1-\mathbf{R}_\nu\right)\frac{e^2}{\left|\mathbf{r}_1-\mathbf{r}_2\right|}\phi_{i'}^{*}\left(\mathbf{r}_2-\mathbf{R}_{\mu'}\right)\phi_{j'}^{*}\left(\mathbf{r}_2-\mathbf{R}_{\nu'}\right)$$

multi-center electron repulsion integrals

Example: Density of states (DOS) for a Li_{24} cluster





$$\rho_\sigma(\varepsilon) = \frac{1}{N\pi} \sum_{k=1}^{N_{MO}} \frac{\Gamma}{\left[\varepsilon - \tilde{\varepsilon}_{k\sigma}(t)\right]^2 + \Gamma^2}$$

$\Gamma = 0.3$ eV

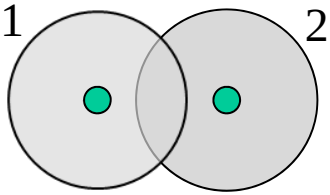
- Broadening of discrete MO levels produces continuous DOS which mimics the energy-band structure of the bulk system.

- Computation of DOS at higher energies requires more atomic orbitals (3s,3p,3d, ...).

Alternative picture: Valence-bond method

$$\left| L_1 M_{L1} S_1 M_{s1}; L_2 M_{L2} S_2 M_{s2} \right\rangle$$

atom 1 atom 2



NOT a one-electron picture

Example: Hg_2

dissociation limit $r \to \infty$

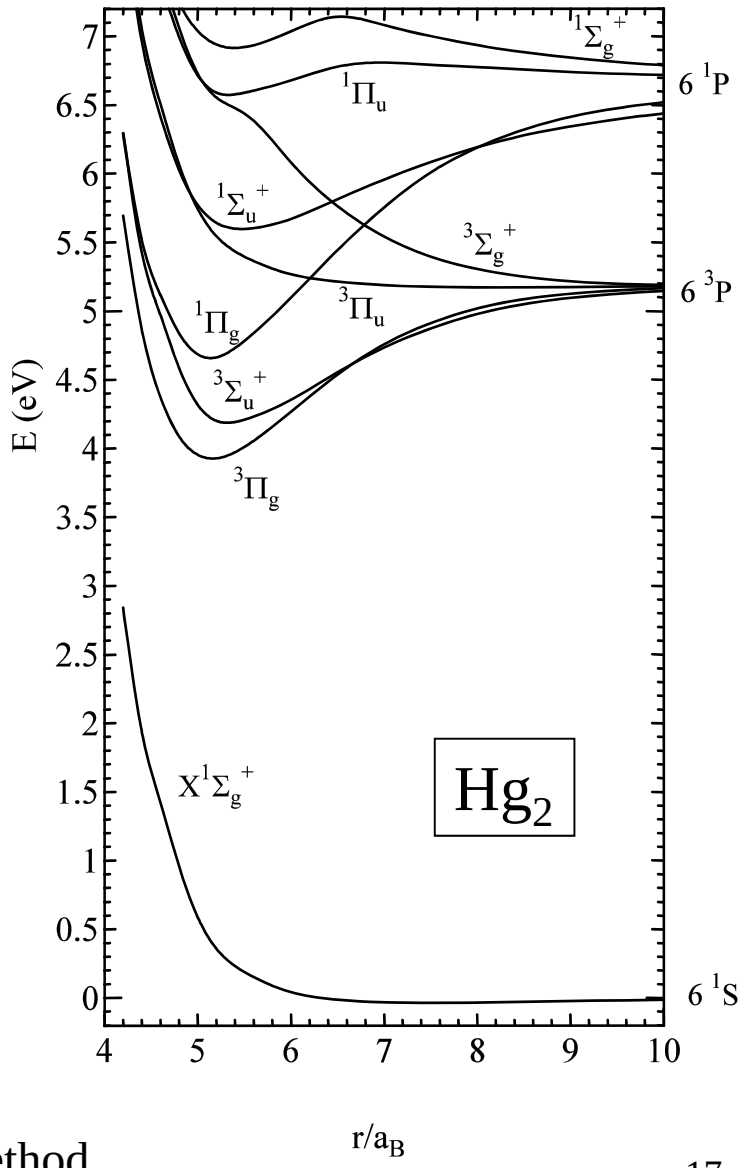
$$\left| X\,{}^1\Sigma_g^{(0)} \right\rangle = \left| {}^1S\,{}^1S;\ 0000;0000 \right\rangle \quad \textbf{ground state}$$

$$\left| {}^1\Sigma_g^{(0)} \right\rangle = \frac{1}{\sqrt{2}}\left(\left| {}^1S\,{}^1P_z;\ 0000;100M_S^z \right\rangle - \left| {}^1P_z\,S;\ 100M_S;0000 \right\rangle \right) \quad \textbf{excited state}$$

↓ configuration mixing (r : finite)

$$\left| X\,{}^1\Sigma_g \right\rangle = \frac{1}{\sqrt{1+\xi_{ij}^2}} \left| X\,{}^1\Sigma_g^{(0)} \right\rangle + \frac{\xi_{ij}}{\sqrt{1+\xi_{ij}^2}} \left| {}^1\Sigma_g^{(0)} \right\rangle$$

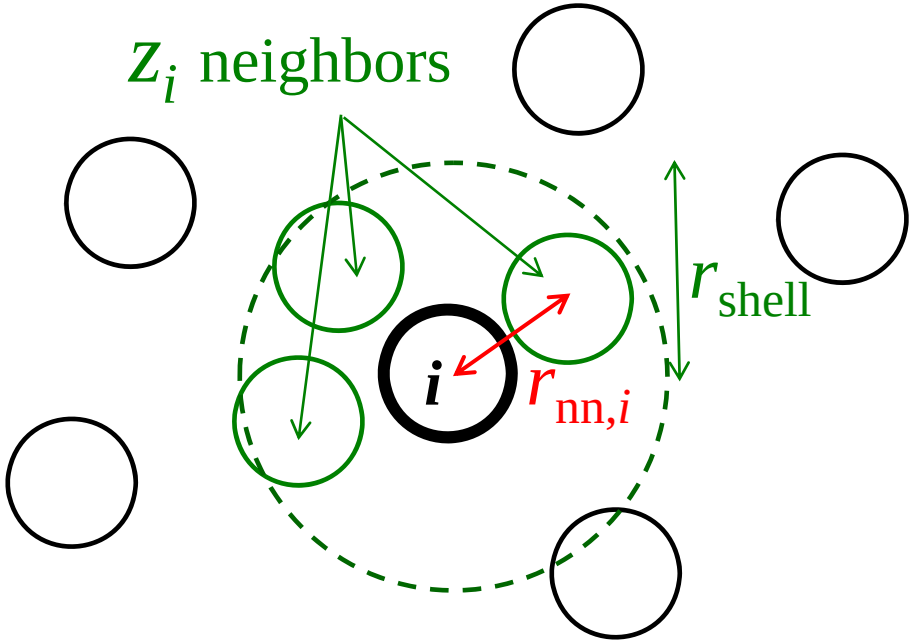
$$E = \left\langle X\,{}^1\Sigma_g \left| H \right| X\,{}^1\Sigma_g \right\rangle \quad \textbf{total energy}$$



Application to clusters: diatomics-in-molecules (DIM) method

3. Equation of state for mercury

Temporary 'clustering' in a fluid



local environment of *i*th atom:

- z_i : coordination number
- $r_{\text{nn},i}$: nearest-neighbor distance

***many-body* potential**

$$V(\mathbf{R}_1,\cdots,\mathbf{R}_N)=\frac{1}{2}\sum_{i,j=1(i\neq j)}^{N} V_{\text{dimer}}\left(\left|\mathbf{R}_i-\mathbf{R}_j\right|\right)+V_{\text{mb}}(\mathbf{R}_1,\cdots,\mathbf{R}_N)$$

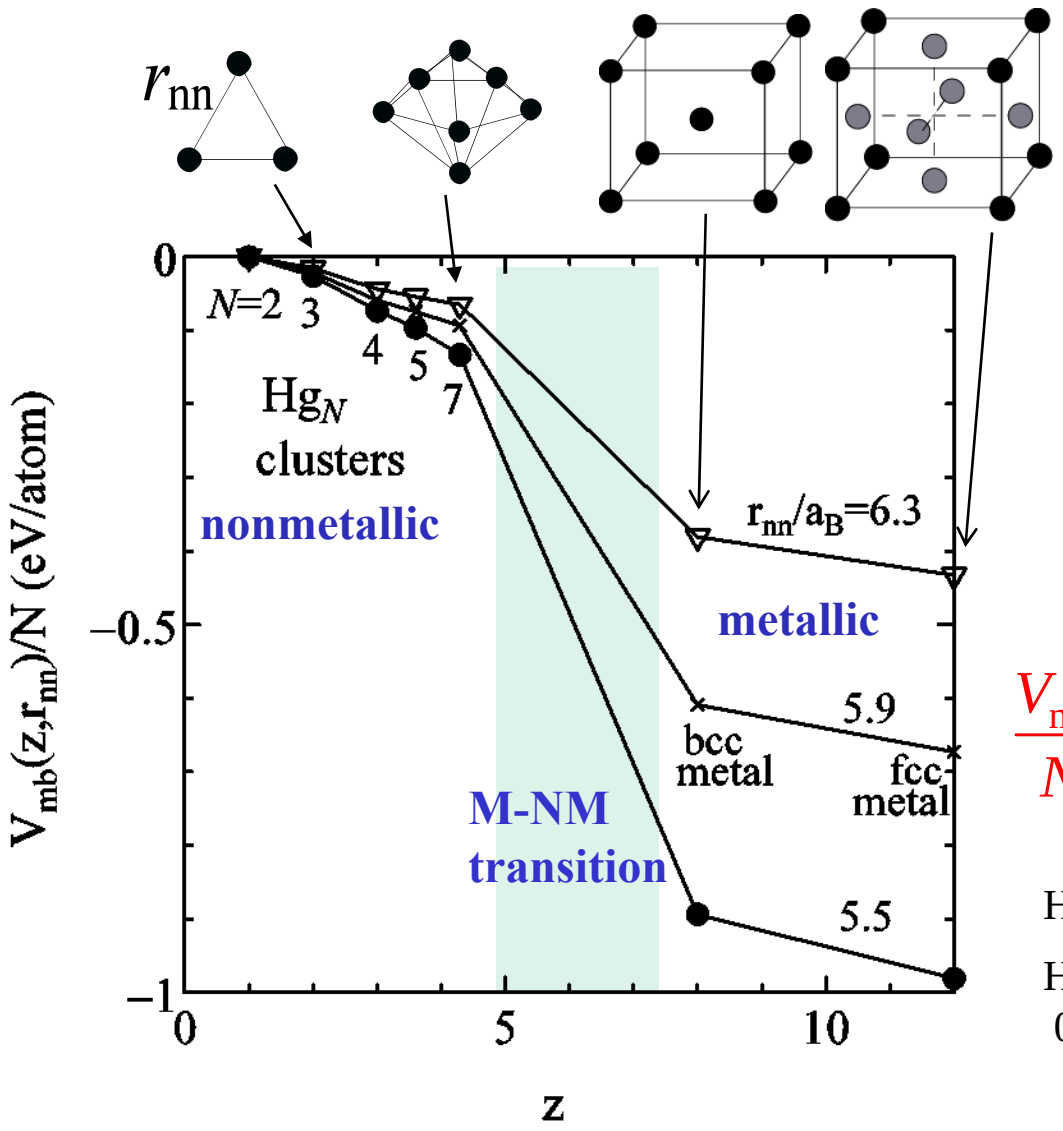
total potential energy

atom-atom potential

approximation

$$\sum_{i=1}^{N}\frac{V_{\text{mb}}}{N}(z_i,r_{\text{nn},i})$$

$V_{mb}(z,r_{nn})/N$ for Hg_N clusters and solids



z : coordination number

r_{nn} : nearest-neighbor distance

diatomics-in-molecules (DIM) cluster calculation
+
modified nearly-free-electron model of solids

$\frac{V_{mb}}{N} < 0$! (attractive)

H. K., Chem. Phys. Lett. **425**, 205 (2006)

H. K., J. Phys.: Condens. Matter **19**, 072102 (2007)

Helmholtz free energy

$$F \le F_{\mathrm{HS}} + \left\langle H - H_{\mathrm{HS}} \right\rangle_{\mathrm{HS}}$$ Gibbs-Bogoliubov inequality

pair-distribution function *soft-sphere correction*

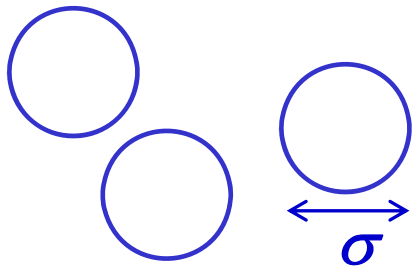
$$\frac{F(n,T;\sigma)}{N} = \frac{F_{\mathrm{HS}}(\sigma)}{N} + \frac{n}{2}\int_{\sigma}^{\infty} dr\, 4\pi r^2 V_{\mathrm{dimer}}(r)\, g_{\mathrm{HS}}(r) + f_6(\sigma)$$

$$+ \sum_{z=1}^{12} p_{\mathrm{HS}}(z) \left[\int_{\sigma}^{r_{shell}} dr_{\mathrm{nn}}\, H_{\mathrm{HS}}(r_{\mathrm{nn}}) \frac{V_{\mathrm{mb}}(z, r_{\mathrm{nn}})}{N} \right]$$

distribution functions of z and r_{nn}

$$\frac{\partial F(n,T;\sigma)}{\partial \sigma} = 0$$ σ optimized

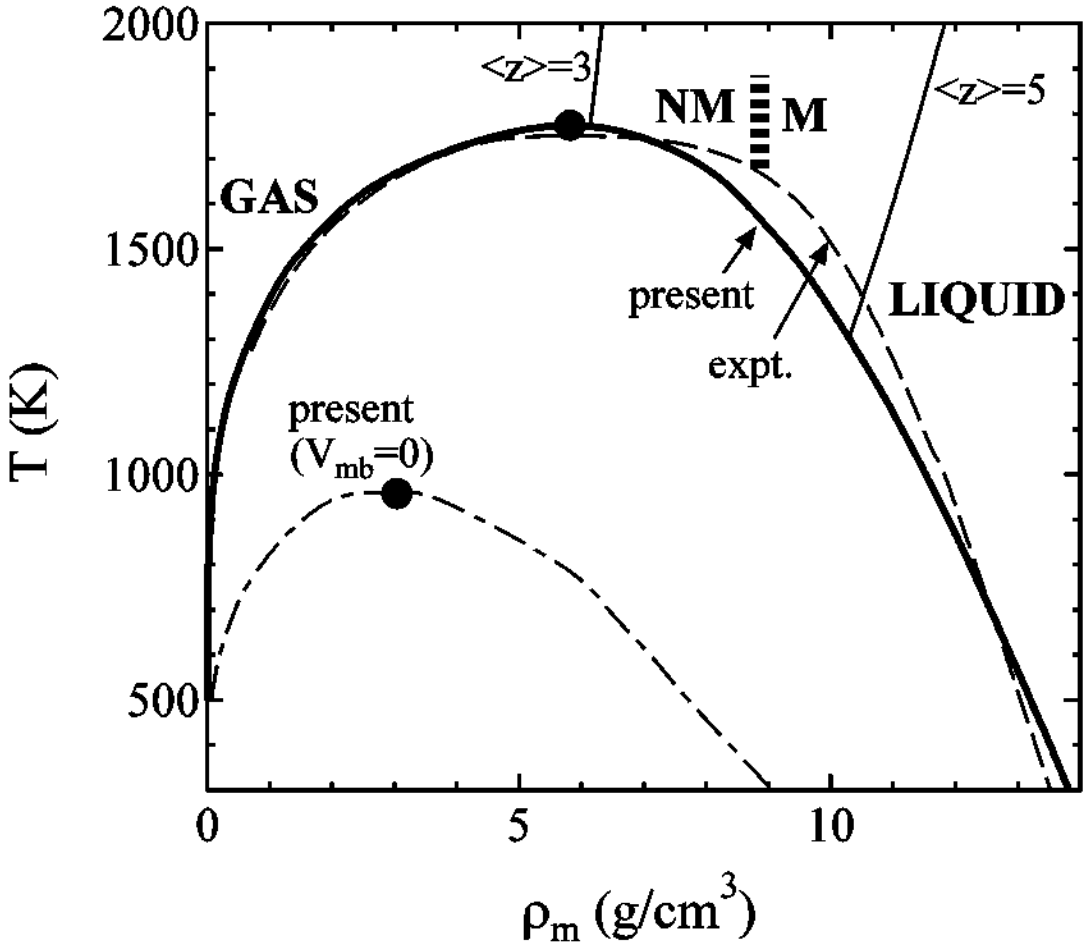
$$\Rightarrow \quad P = n^2 \left(\frac{\partial (F/N)}{\partial n} \right)_T$$ equation of state



hard-sphere (HS) reference system

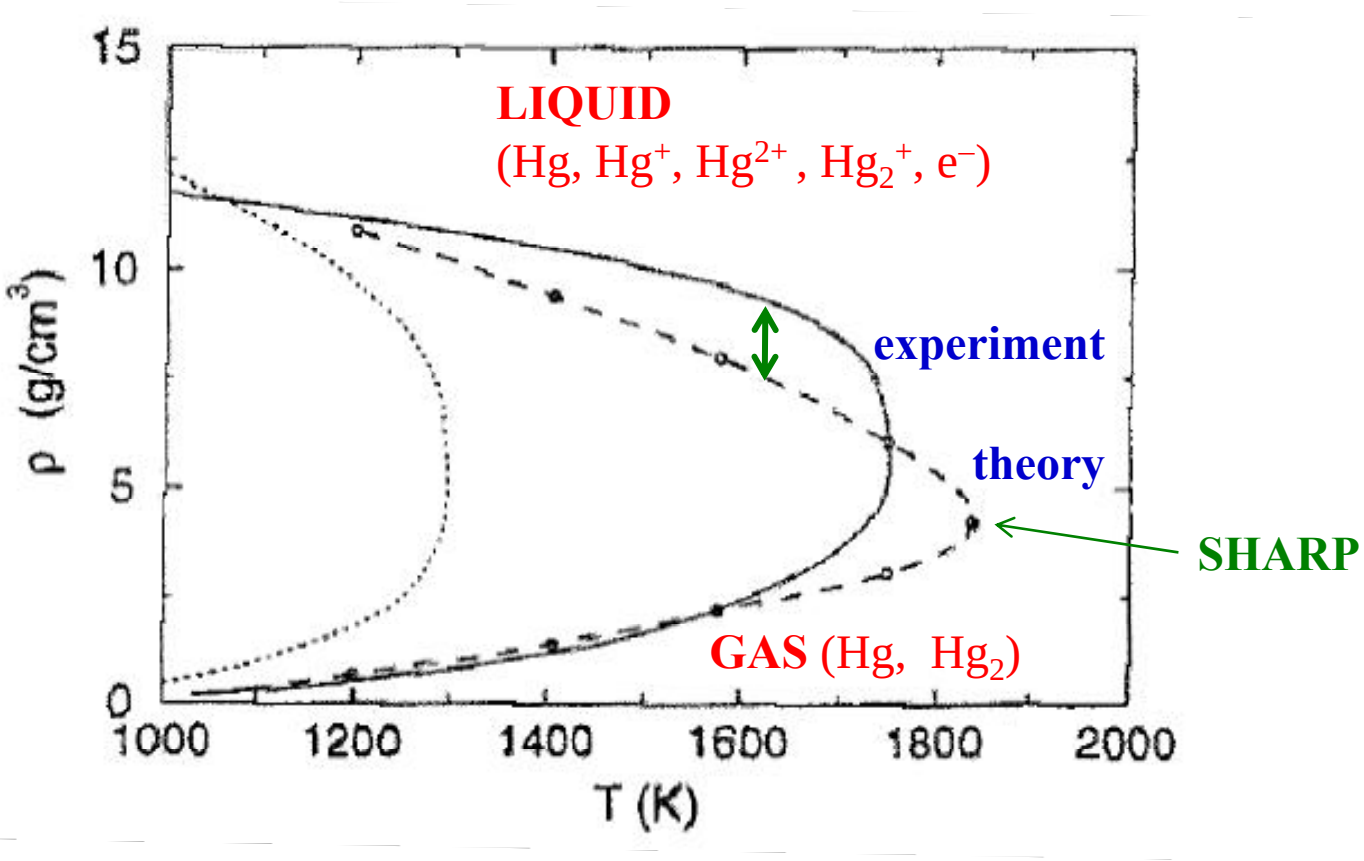
H. K., J. Chem. Phys. **126**, 134509 (2007)

Numerical result: Coexistence curve of Hg



H. K., J. Chem. Phys. **126**, 134509 (2007)

Comparison with the plasma model

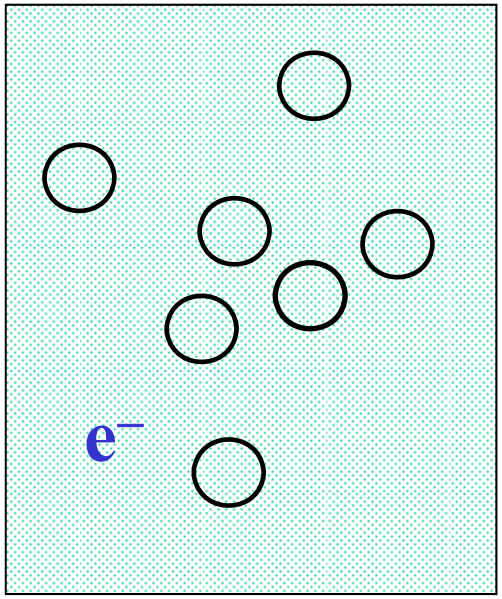


Chemical equilibrium of atoms, ions, molecules, electrons

R. Redmer, Phys. Rep. **282**, 35 (1997)

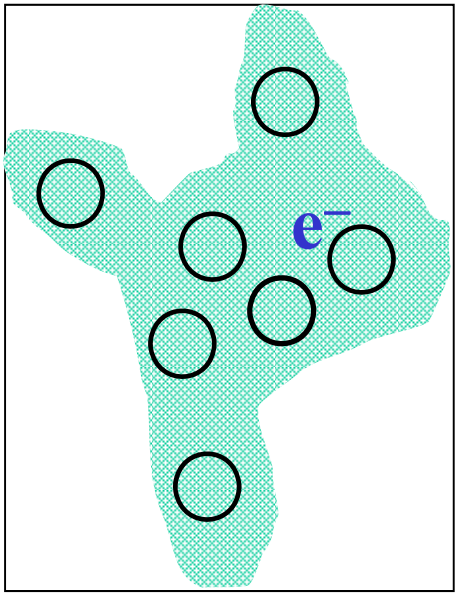
Electron distributions in expanded metals

plasma picture



homogeneous

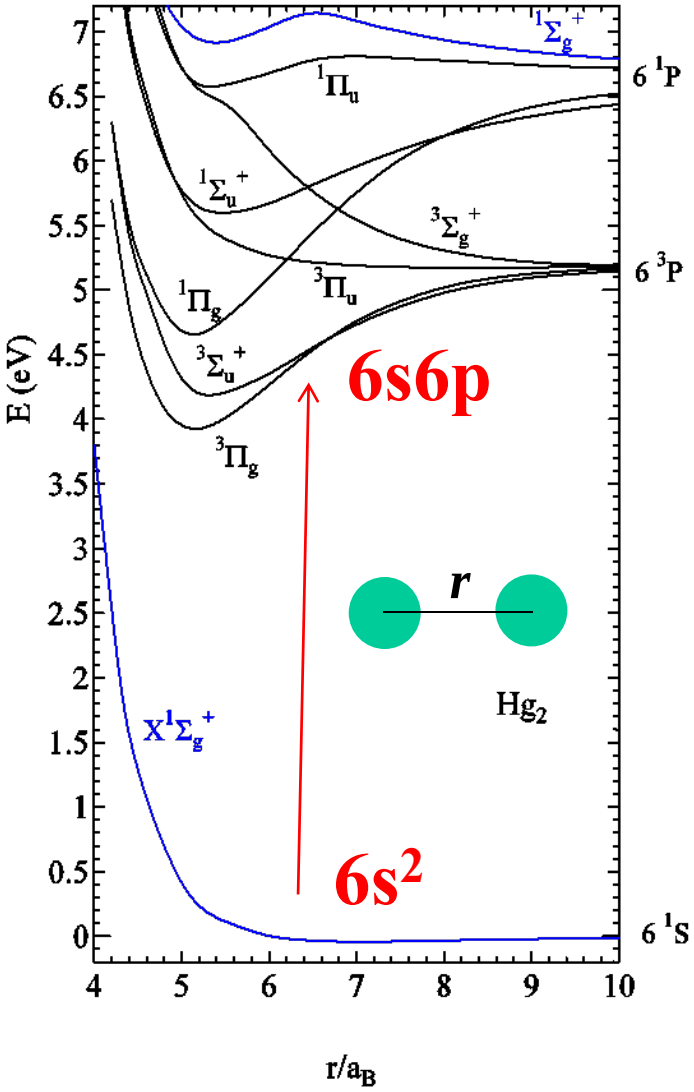
condensed-matter picture

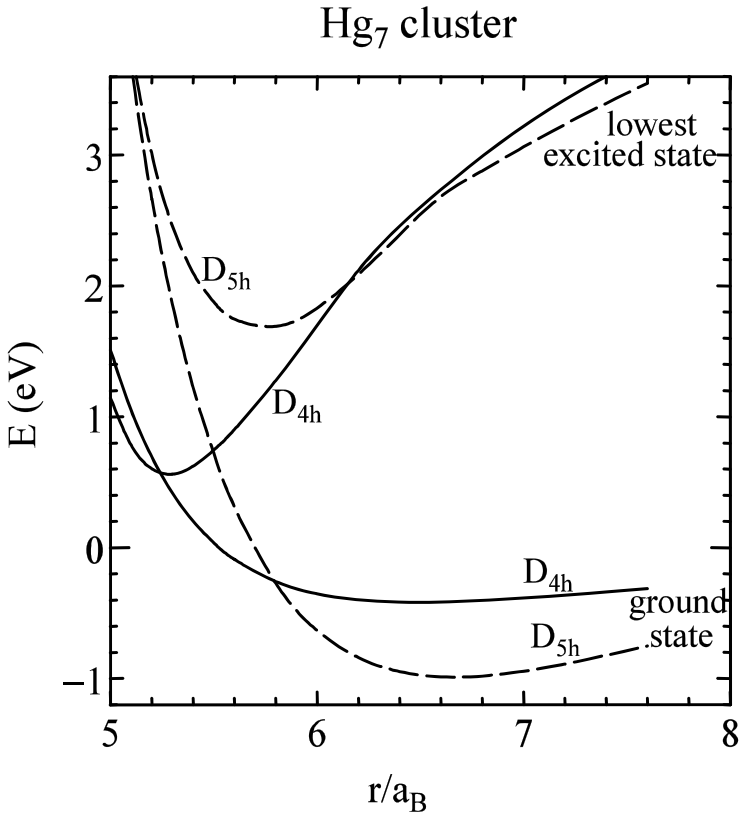


inhomogeneous

(→supported by QMD simulations)

What happens at higher temperatures ?





stronger binding in excited states

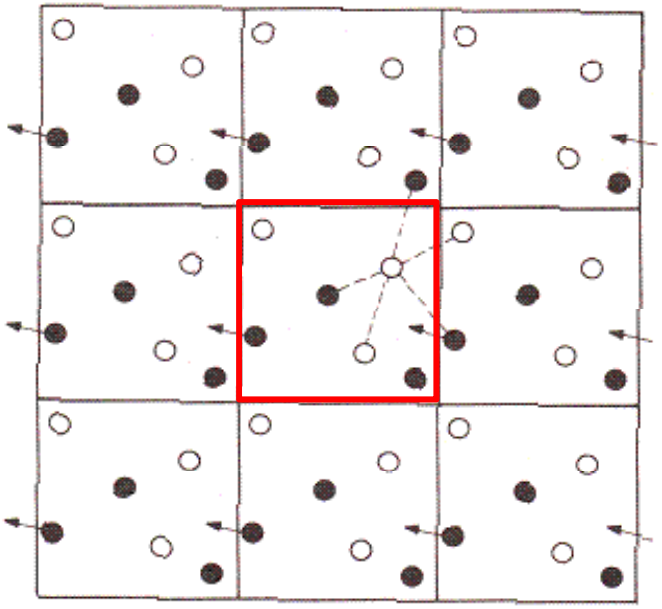
➡ **reduction of pressures** ?

Czuchaj, Rebentrost, Stoll & Preuss,
Chem. Phys. **214**, 277 (1997)

4. *Ab initio* molecular dynamics

Quantum molecular dynamics (QMD) simulation (*Ab initio*)

periodic supercell



nuclei at $\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N$

↓ ***density-functional theory (DFT)***

electron wave function $\psi_{\boldsymbol{ki}}(r)$
potential energy $V(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N)$

↓ statistical average ***molecular dynamics (MD)***

thermodynamics
correlation functions
conductivities
…….

R. Car & M. Parrinello:
Phys. Rev. Lett. **55** (1985) 2471

M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias & J.D. Joannopoulos:
Rev. Mod. Phys. **64** (1992) 1045

Total potential energy in DFT

$$V(\mathbf{R}_1,\cdots,\mathbf{R}_N)=\sum_{\mathbf{k},i}\int d\mathbf{r}\psi^*_{\mathbf{k},i}(\mathbf{r})\left[-\frac{\hbar^2}{2m_e}\nabla^2+\sum_{\mu=1}^{N}V_{ei}(\mathbf{r}-\mathbf{R}_\mu)\right]\psi_{\mathbf{k},i}(\mathbf{r})$$

$$+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}+E_{xc}[n(\mathbf{r})]+\frac{1}{2}\sum_{\substack{\mu,\nu=1\\(\mu\neq\nu)}}^{N}\frac{Z_\mu Z_\nu e^2}{|\mathbf{R}_\mu-\mathbf{R}_\nu|}$$

exchange-correlation energy functional (not known exactly)

electron density

$$n(\mathbf{r})=\sum_{\mathbf{k}}^{\mathrm{BZ}}\sum_{i}f(\varepsilon_{\mathbf{k},i})\left|\psi_{\mathbf{k},i}(\mathbf{r})\right|^2$$

band index ← ; **Fermi distribution** ←

Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2+\sum_{\mu=1}^{N}V_{ei}(\mathbf{r}-\mathbf{R}_\mu)+\int d\mathbf{r}'\frac{n(\mathbf{r}')e^2}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}\right]\psi_{\mathbf{k},i}(\mathbf{r})=\varepsilon_{\mathbf{k},i}\psi_{\mathbf{k},i}(\mathbf{r})$$

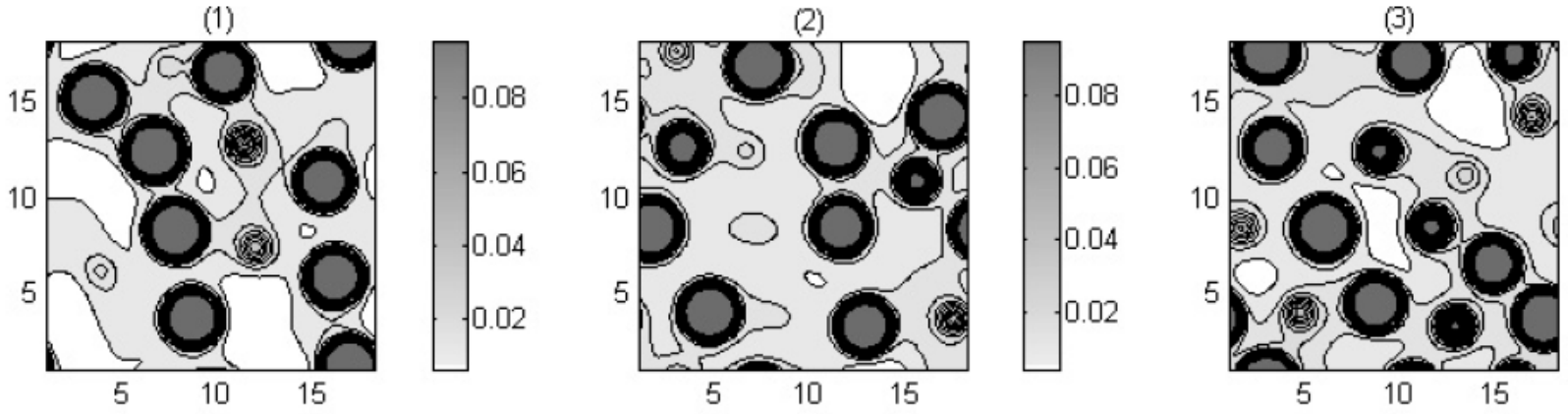
W. Kohn, Nobel Prize in Chemistry, 1998

Charge density map in fluid Rb

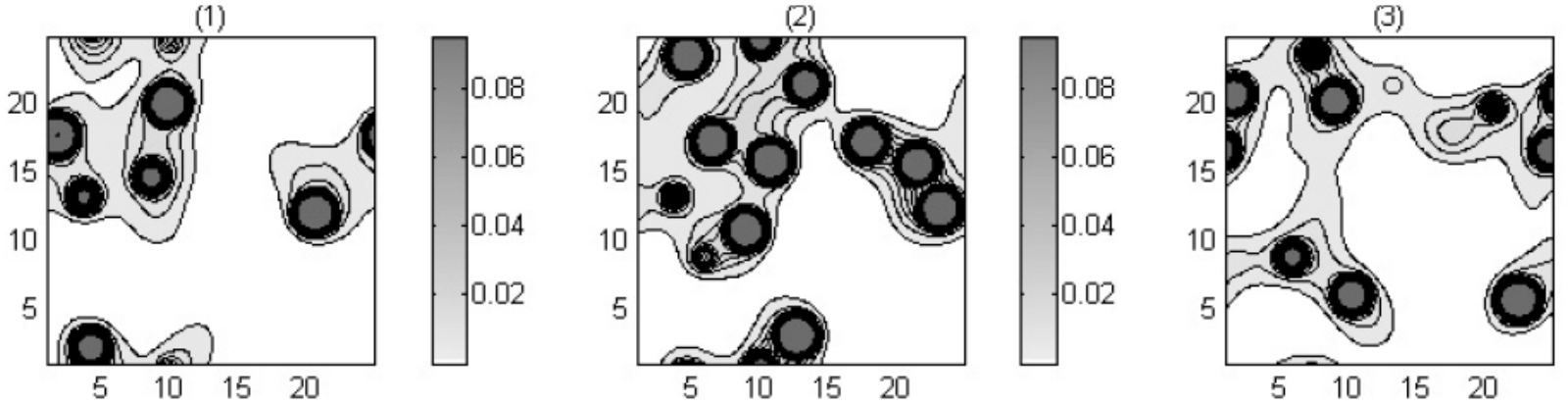
64 atoms, 5-20 ps

Kietzmann, Redmer, Hensel, Desjarlais & Mattson: J. Phys.:Condens. Matter **18** (2006) 5597

1.5 g/cm^3
373 K
(normal liquid)



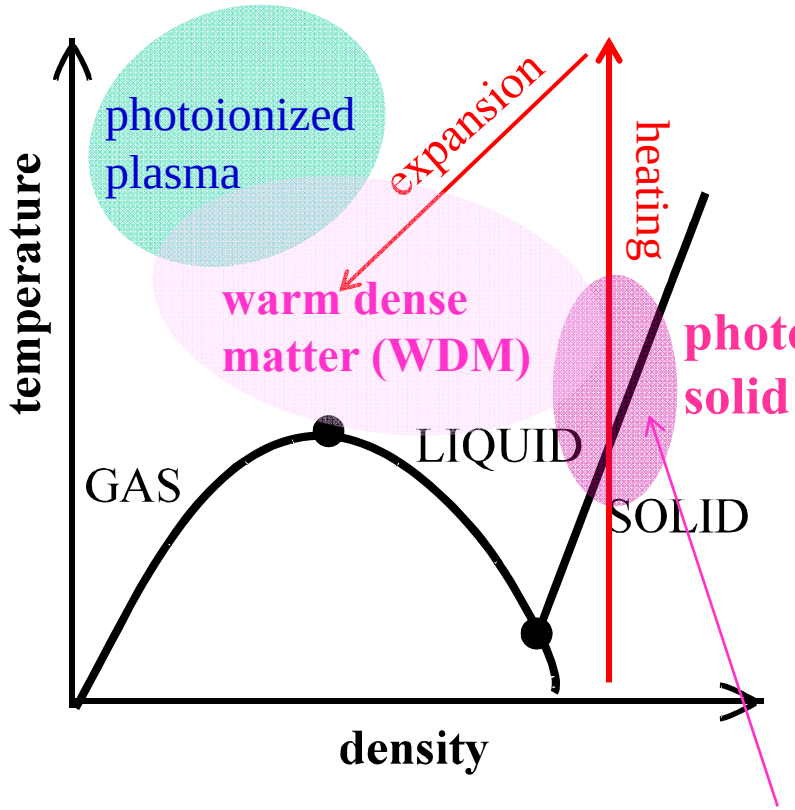
0.59 g/cm^3
2123 K
(expanded)



- Inhomogeneous atomic distributions: transient dimers & trimers

5. Photoexcitation kinetics of solids

Heating of solid targets by ultrashort-pulse lasers



Initially, electrons are heated at constant density.

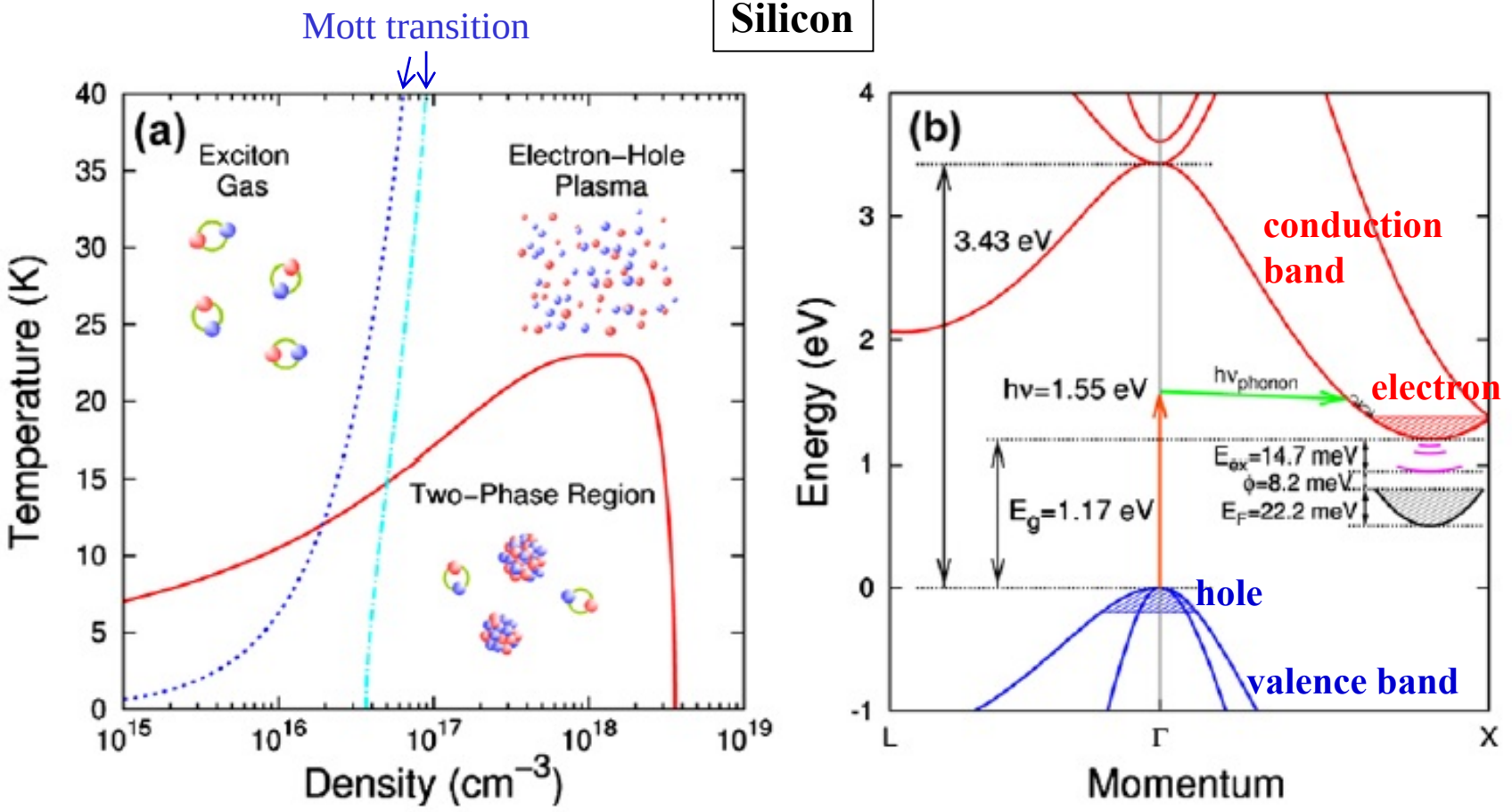
How can we simulate highly photoexcited solids?

- modification of electronic structures in excited states
- electron-hole correlation
- dynamics of collisional/radiative transitions

Electron-hole liquid (EHL) in a photoexcited semiconductor

Prototypical system of highly excited condensed matter

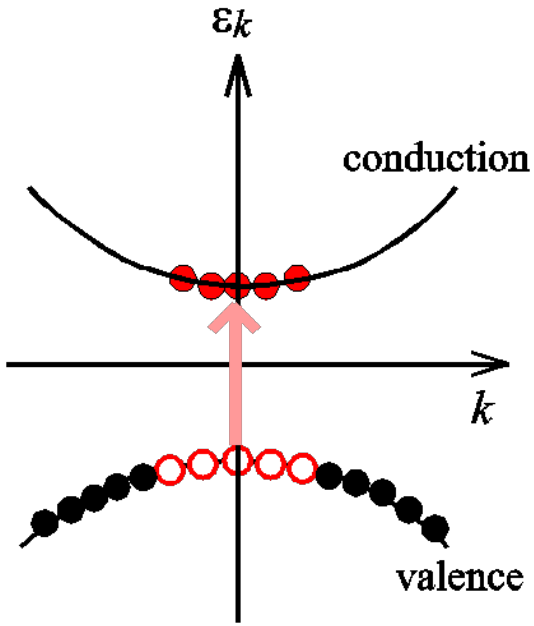
Silicon



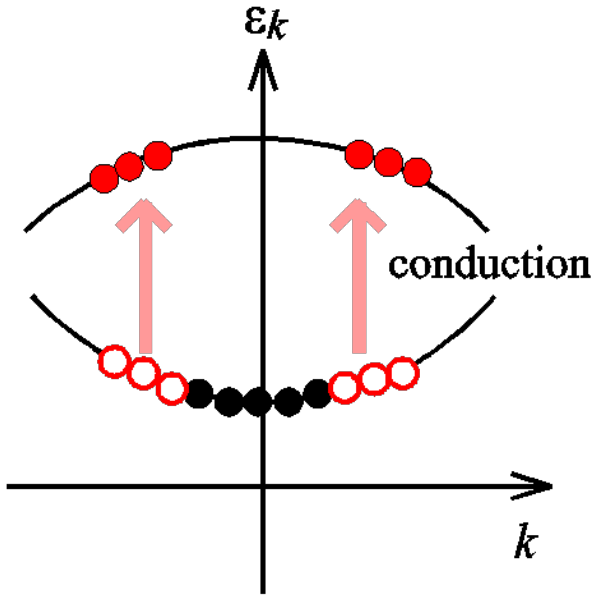
T. Suzuki & R. Shimano, Phys. Rev. Lett. **103**, 057401 (2009)

Various types of photoexcited solids

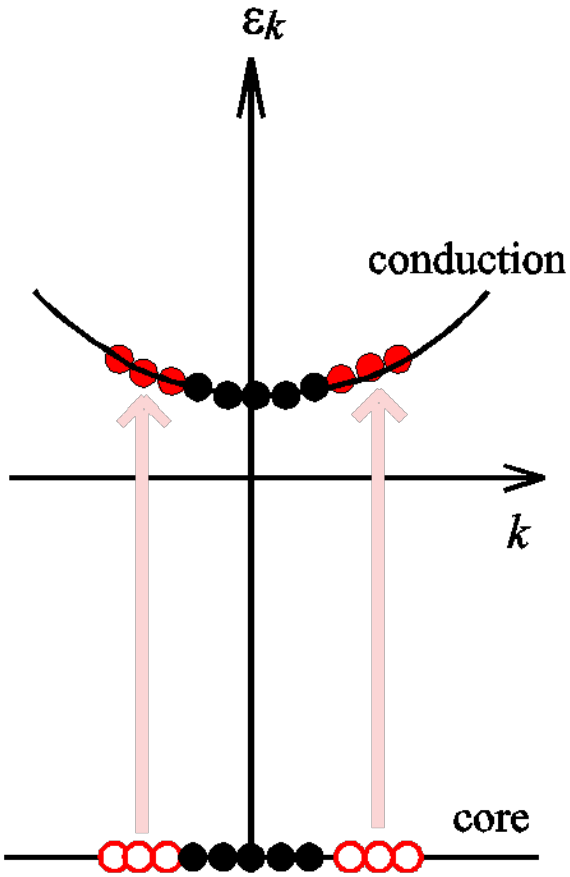
EHL
(semiconductor)



WDM
(metal, visible light)



'Hollow-atom solid'
(metal, EUV or X-ray)



Hamiltonian (electron, phonon, photon)

P. Fulde, *Electron Correlations in Molecules and Solids* (Springer, 1995), Chap. 2

Hartree-Fock one-electron energy

Hartree exchange

$$H = \sum_{k\sigma} \varepsilon_k^{\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} - \sum_{k_1 k_2 \sigma} \sum_{k_3 \sigma'} \left(V_{k_1 k_2 k_3 k_3}^{\sigma\sigma'} - \delta_{\sigma\sigma'} V_{k_1 k_3 k_3 k_2}^{\sigma\sigma} \right) \delta_{k_3\sigma'}^{\mathrm{occ}} c_{k_1\sigma}^{\dagger} c_{k_2\sigma}$$

$$+ \frac{1}{2} \sum_{\substack{k_1 k_2 k_3 k_4 \\ \sigma\sigma'}} V_{k_1 k_2 k_3 k_4}^{\sigma\sigma'} c_{k_1\sigma}^{\dagger} c_{k_3\sigma'}^{\dagger} c_{k_4\sigma'} c_{k_2\sigma} + \frac{e}{m_e c} \mathbf{A}(t) \sum_{k_1 k_2 \sigma} \mathbf{p}_{k_1 k_2}^{\sigma} c_{k_1\sigma}^{\dagger} c_{k_2\sigma} + \sum_{k_1 k_2 \sigma} U_{k_1 k_2}^{\sigma} c_{k_1\sigma}^{\dagger} c_{k_2\sigma}$$

e-e collision photoabsorption & emission **e-phonon interaction**

+ $\mathbf{A}^2(t)$-term (scattering of photons)

$$\delta_{k_1\sigma_1}^{\mathrm{occ}} \equiv \begin{cases} 1 & \text{if state } (k_1, \sigma_1) \text{ is occupied in the ground state} \\ 0 & \text{otherwise} \end{cases}$$

$$V_{k_1 k_2 k_3 k_4}^{\sigma_1\sigma_2} \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_{k_1}^{\sigma_1 *}(\mathbf{r}_1) \psi_{k_2}^{\sigma_1}(\mathbf{r}_1) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{k_3}^{\sigma_2 *}(\mathbf{r}_2) \psi_{k_4}^{\sigma_2}(\mathbf{r}_2)$$ electron repulsion integral

$$\mathbf{p}_{k_1 k_2}^{\sigma} \equiv \int d\mathbf{r} \psi_{k_1}^{\sigma *}(\mathbf{r}) \frac{\hbar}{i} \nabla \psi_{k_2}^{\sigma}(\mathbf{r})$$ momentum operator

$$\mathbf{A}(t) = \frac{1}{2} \mathbf{A}_0 \exp(-i\omega_\nu t) + \mathrm{cc}$$ vector potential of the laser field

Density matrix equation for electron transitions

$c_{k\sigma}^{\dagger}$, $c_{k\sigma}$: creation & annihilation operators of an electron in state (k, σ)

$$\left\{c_{k\sigma}^{\dagger},\ c_{k'\sigma'}\right\}=\delta_{kk'}\delta_{\sigma\sigma'},\ \left\{c_{k\sigma}^{\dagger},\ c_{k'\sigma'}^{\dagger}\right\}=\left\{c_{k\sigma},\ c_{k'\sigma'}\right\}=0$$ anticommutation relations

$\left\langle \rho_{kk'\sigma}\right\rangle \equiv\left\langle c_{k\sigma}^{\dagger}c_{k'\sigma}\right\rangle$: one-particle density matrix

$\left\langle \cdots\right\rangle$: expectation value

$$i\hbar\frac{\partial}{\partial t}\left\langle \rho_{kk'\sigma}(t)\right\rangle =\left\langle \left[c_{k\sigma}^{\dagger}c_{k'\sigma},H(t)\right]\right\rangle$$ quantum-mechanical equation of motion

$\left\langle \rho_{kk\sigma}(t)\right\rangle = f_{k\sigma}(t)$ diagonal element = population of kth MO

$\left\langle \rho_{kk'\sigma}(t)\right\rangle (k\neq k')$ off-diagonal element = polarization

→ Successfully applied to photoexcited semiconductors

"Semiconductor Bloch equation"

F. Rossi & T. Kuhn, *Rev. Mod. Phys.* **74** 895 (2002)

→ In principle, applicable to photoexcited WDM

Off-diagonal elements

$$i\hbar\frac{\partial}{\partial t}\langle\rho_{kk'\sigma}(t)\rangle=\left(\varepsilon_{k'}^{\sigma}-\varepsilon_{k}^{\sigma}\right)\langle\rho_{kk'\sigma}(t)\rangle$$
$$+\sum_{k_3}\left[\left(\tilde{\varepsilon}_{k'k_3\sigma}(t)+\frac{e}{m_e c}\mathbf{A}(t)\cdot\mathbf{p}_{k'k_3}^{\sigma}+U_{k'k_3}^{\sigma}\right)\langle\rho_{kk_3\sigma}(t)\rangle-\left(\tilde{\varepsilon}_{k_3k\sigma}(t)+\frac{e}{m_e c}\mathbf{A}(t)\cdot\mathbf{p}_{k_3k}^{\sigma}+U_{k_3k}^{\sigma}\right)\langle\rho_{k_3k'\sigma}(t)\rangle\right]$$
$$+i\hbar\frac{\partial}{\partial t}\langle\rho_{kk'\sigma}(t)\rangle\Big]_{\text{coll}}$$

$$\tilde{\varepsilon}_{kk'\sigma}(t)\equiv\sum_{k_1k_2\sigma_1}\left(V_{kk'k_1k_2}^{\sigma\sigma_1}-\delta_{\sigma\sigma_1}V_{kk_2k_1k'}^{\sigma\sigma}\right)\left[\langle\rho_{k_1k_2\sigma_1}(t)\rangle-\delta_{k_1k_2}\delta_{k_1\sigma_1}^{\text{occ}}\right]$$

self-energy matrix
(energy-level shift)

$$i\hbar\frac{\partial}{\partial t}\langle\rho_{kk'\sigma}(t)\rangle\Big]_{\text{coll}}=\sum_{k_1k_2k_3\sigma_1}\left(V_{k'k_3k_1k_2}^{\sigma\sigma_1}\delta K_{kk_3k_1k_2}^{\sigma\sigma_1}(t)-V_{k_3kk_2k_1}^{\sigma\sigma_1}\delta K_{k_3k'k_2k_1}^{\sigma\sigma_1}(t)\right)$$

collision term
(electron correlation)

(cf. lecture by T. Bell)

$$K_{kk_3k_1k_2}^{\sigma\sigma_1}\equiv\langle c_{k\sigma}^{\dagger}c_{k_1\sigma_1}^{\dagger}c_{k_2\sigma_1}c_{k_3\sigma}\rangle$$

two-particle density matrix

$$\equiv\underbrace{\langle\rho_{kk_3\sigma}\rangle\langle\rho_{k_1k_2\sigma_1}\rangle-\delta_{\sigma\sigma_1}\langle\rho_{k_1k_3\sigma}\rangle\langle\rho_{kk_2\sigma}\rangle}_{\text{H-F}}+\delta K_{kk_3k_1k_2}^{\sigma\sigma_1}$$

correlation part

Approximation 1: Two-state approximation $(k_3 = k, k')$

$$i\hbar \frac{\partial}{\partial t}\left\langle \rho_{kk'\sigma}(t)\right\rangle \cong \left[\left(\underbrace{\varepsilon_{k'}^{\sigma} + \tilde{\varepsilon}_{k'k'\sigma}(t)}_{\text{renormalized energy level}} + \frac{e}{m_e c}\underbrace{\mathbf{A}(t)\cdot\mathbf{p}_{k'k'}^{\sigma}}_{\text{intraband transition (Drude)}}\right) - \left(\varepsilon_{k}^{\sigma} + \tilde{\varepsilon}_{kk\sigma}(t) + \frac{e}{m_e c}\mathbf{A}(t)\cdot\mathbf{p}_{kk}^{\sigma}\right)\right]\left\langle \rho_{kk'\sigma}(t)\right\rangle$$

$$+\left(\underbrace{\tilde{\varepsilon}_{k'k\sigma}(t)}_{\text{induced field}} + \frac{e}{m_e c}\mathbf{A}(t)\cdot\mathbf{p}_{k'k}^{\sigma} + U_{k'k}^{\sigma}\right)\left[f_{k\sigma}(t) - f_{k'\sigma}(t)\right] \qquad k\text{-}k'\text{ transition}$$

$$+i\hbar \frac{\partial}{\partial t}\left\langle \rho_{kk'\sigma}(t)\right\rangle\Big]_{\text{coll}}$$

⟶ Solved within the Markov approximation, assuming that $\left\langle \rho_{kk'\sigma}(t)\right\rangle$ varies more rapidly than $f_{k\sigma}(t)$.

Approximation 2: Born approximation to the collision term

$$i\hbar\frac{\partial \delta K^{\sigma\sigma_1}_{kk_3k_1k_2}}{\partial t} = \left(\varepsilon^{\sigma}_{k_3} + \varepsilon^{\sigma_1}_{k_2} - \varepsilon^{\sigma_1}_{k_1} - \varepsilon^{\sigma}_{k}\right)\delta K^{\sigma\sigma_1}_{kk_3k_1k_2} + S^{\sigma\sigma_1}_{kk_3k_1k_2}$$

$$S^{\sigma\sigma_1}_{kk_3k_1k_2} \cong \sum_{k_4k_5k_6k_7} V^{\sigma\sigma_4}_{k_4k_5k_6k_7}\Big[\left\langle\rho_{kk_5\sigma}\right\rangle\left\langle\rho_{k_1k_7\sigma_1}\right\rangle\left(\left\langle\rho_{k_6k_2\sigma_1}\right\rangle - \delta_{k_6k_2}\right)\left(\left\langle\rho_{k_4k_3\sigma}\right\rangle - \delta_{k_4k_3}\right)$$
$$-\left(\left\langle\rho_{kk_5\sigma}\right\rangle - \delta_{kk_5}\right)\left(\left\langle\rho_{k_1k_7\sigma_1}\right\rangle - \delta_{k_1k_7}\right)\left\langle\rho_{k_6k_2\sigma_1}\right\rangle\left\langle\rho_{k_4k_3\sigma}\right\rangle\Big]$$

$$\cong V^{\sigma\sigma_3}_{k_3k'k_2k_1}\Big[\, f_{k_1\sigma_1}(1-f_{k_2\sigma_1})(1-f_{k_3\sigma}) + (1-f_{k_1\sigma_1})\, f_{k_2\sigma_1}\, f_{k_3\sigma}\Big]\left\langle\rho_{kk'\sigma}\right\rangle$$

↑ dominant term

→ varies slowly with t **(Markov approximation)**

$$\left.\frac{\partial}{\partial t}\left\langle\rho_{kk'\sigma}(t)\right\rangle\right]_{\text{coll}} \cong -\frac{1}{i\hbar}\sum_{k_1k_2k_3\sigma_1}\left(\wp\frac{\left|V^{\sigma\sigma_1}_{k'k_3k_1k_2}\right|^2}{\varepsilon^{\sigma}_{k_3} + \varepsilon^{\sigma_1}_{k_2} - \varepsilon^{\sigma_1}_{k_1} - \varepsilon^{\sigma}_{k}} + \wp\frac{\left|V^{\sigma\sigma_1}_{k_3kk_2k_1}\right|^2}{\varepsilon^{\sigma}_{k'} + \varepsilon^{\sigma_1}_{k_1} - \varepsilon^{\sigma_1}_{k_2} - \varepsilon^{\sigma}_{k_3}}\right)$$
$$\times\Big[\, f_{k_1\sigma_1}(1-f_{k_2\sigma_1})(1-f_{k_3\sigma}) + (1-f_{k_1\sigma_1})\, f_{k_2\sigma_1}\, f_{k_3\sigma}\Big]\left\langle\rho_{kk'\sigma}\right\rangle$$
$$-\Gamma\left\langle\rho_{kk'\sigma}(t)\right\rangle \leftarrow \text{relaxation}$$

screening effect on energy-level shift

Diagonal elements

radiative transitions

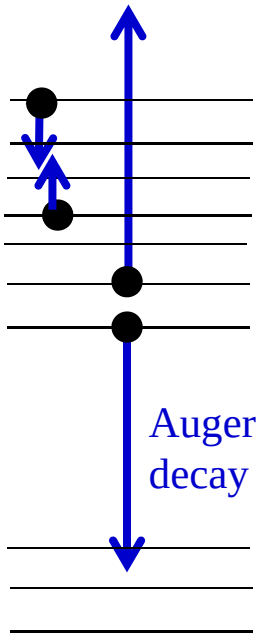
$$i\hbar\frac{\partial f_{k\sigma}(t)}{\partial t}=\sum_{k'(\neq k)}\left[\left(\tilde{\varepsilon}_{kk'\sigma}(t)+\frac{e}{m_e c}\mathbf{A}(t)\cdot\mathbf{p}^{\sigma}_{kk'}+U^{\sigma}_{kk'}\right)\left\langle\rho_{kk'\sigma}(t)\right\rangle-\left(\tilde{\varepsilon}_{k'k\sigma}(t)+\frac{e}{m_e c}\mathbf{A}(t)\cdot\mathbf{p}^{\sigma}_{k'k}+U^{\sigma}_{k'k}\right)\left\langle\rho_{k'k\sigma}(t)\right\rangle\right]$$

$$+i\hbar\frac{\partial f_{k\sigma}(t)}{\partial t}\Big]_{\text{coll}}$$ ← e-e collision

$$\frac{\partial f_{k\sigma}(t)}{\partial t}\Big]_{\text{coll}}=-\frac{1}{\hbar}\sum_{k_1k_2k_3\sigma_1}V^{\sigma\sigma_1}_{kk_3k_1k_2}\left(V^{\sigma\sigma_1}_{k_3kk_2k_1}-\delta_{\sigma\sigma_1}V^{\sigma\sigma}_{k_2kk_3k_1}\right)$$

$$\times\left[f_{k\sigma}f_{k_1\sigma_1}\left(1-f_{k_2\sigma_1}\right)\left(1-f_{k_3\sigma}\right)-\left(1-f_{k\sigma}\right)\left(1-f_{k_1\sigma_1}\right)f_{k_2\sigma_1}f_{k_3\sigma}\right]$$

$$\times\frac{\hbar\Gamma'}{\left(\tilde{\varepsilon}_{k_3\sigma}+\tilde{\varepsilon}_{k_2\sigma_1}-\tilde{\varepsilon}_{k_1\sigma_1}-\tilde{\varepsilon}_{k\sigma}\right)^2+\left(\hbar\Gamma'\right)^2}+\text{cc}$$



Problem: energy conservation, screening

Markov approximation to $\left\langle\rho_{kk'\sigma}(t)\right\rangle$ → **rate equation**

Collisional-radiative rate equation for solids

$$\frac{\partial f_{k\sigma}(t)}{\partial t} = \frac{I_\nu}{\hbar\omega_\nu}\left[\sum_{k'(\neq k)} \sigma_{kk'\sigma}(\omega_\nu)\left[f_{k'\sigma}(t) - f_{k\sigma}(t)\right] - \sigma^{\mathrm{bf}}_{k\sigma}(\omega_\nu) f_{k\sigma}(t)\right]$$

radiative (bound-bound, bound-free)

$$+\left[\frac{1}{\tau^{\mathrm{in}}_{\mathrm{Auger}}(k\sigma)} + \frac{1}{\tau^{\mathrm{in}}_{\mathrm{coll}}(k\sigma)}\right]\left[1 - f_{k\sigma}(t)\right]$$

e-e collision (incoming)

$$-\left[\frac{1}{\tau^{\mathrm{out}}_{\mathrm{Auger}}(k\sigma)} + \frac{1}{\tau^{\mathrm{out,\,cont}}_{\mathrm{Auger}}(k\sigma)} + \frac{1}{\tau^{\mathrm{out}}_{\mathrm{coll}}(k\sigma)}\right] f_{k\sigma}(t)$$

e-e collision (outgoing)

$$I_\nu = \frac{c\left|E_0\right|^2}{8\pi}$$

laser intensity

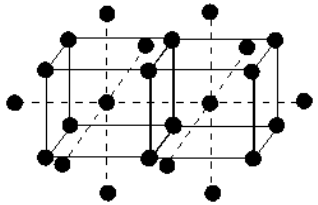
$k = 1, 2, \ldots, N_{\mathrm{MO}}$

($N_{\mathrm{MO}} = NN_{\mathrm{STO}}$)

Rate coefficients include energy-level shifts.

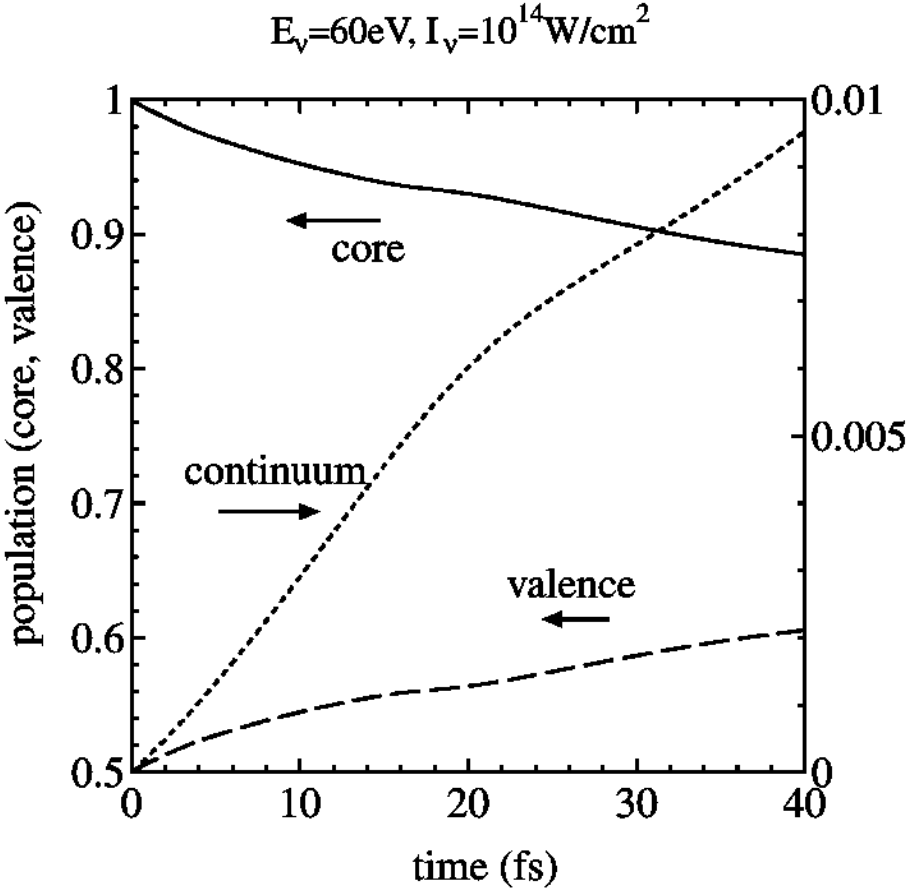
H.K., J. Phys. B **43**, 115601 (2010)

Example: K-edge excitation of lithium by EUV-FEL

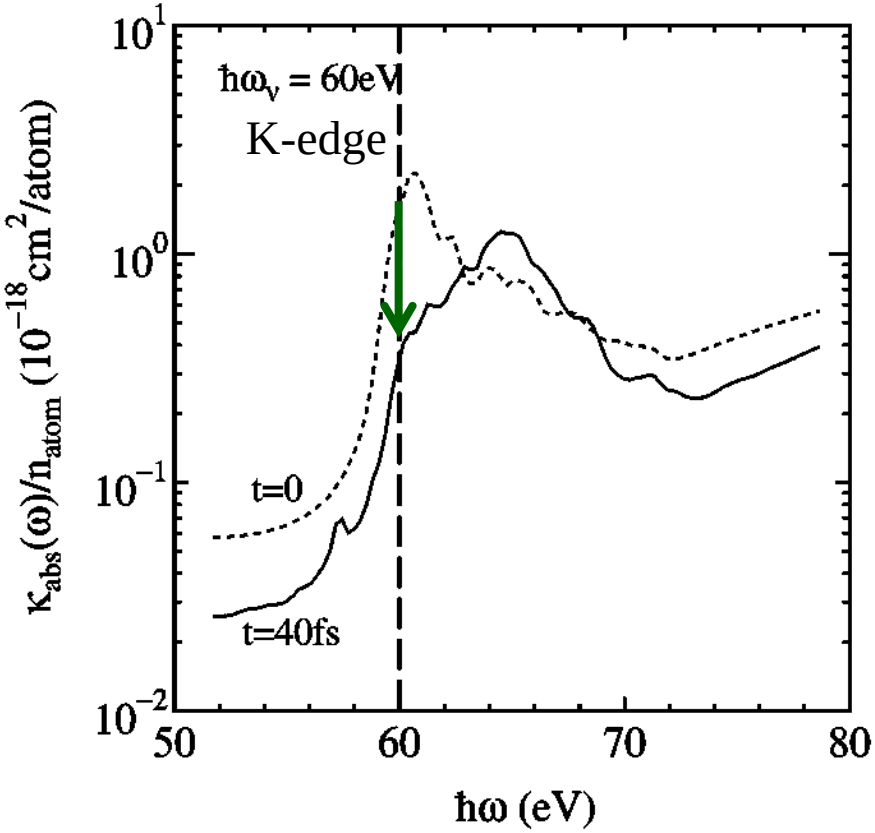


photon energy = 60 eV, intensity = 10^{14} W/cm^2, fixed ions

Population kinetics



Time-resolved photoabsorption spectra

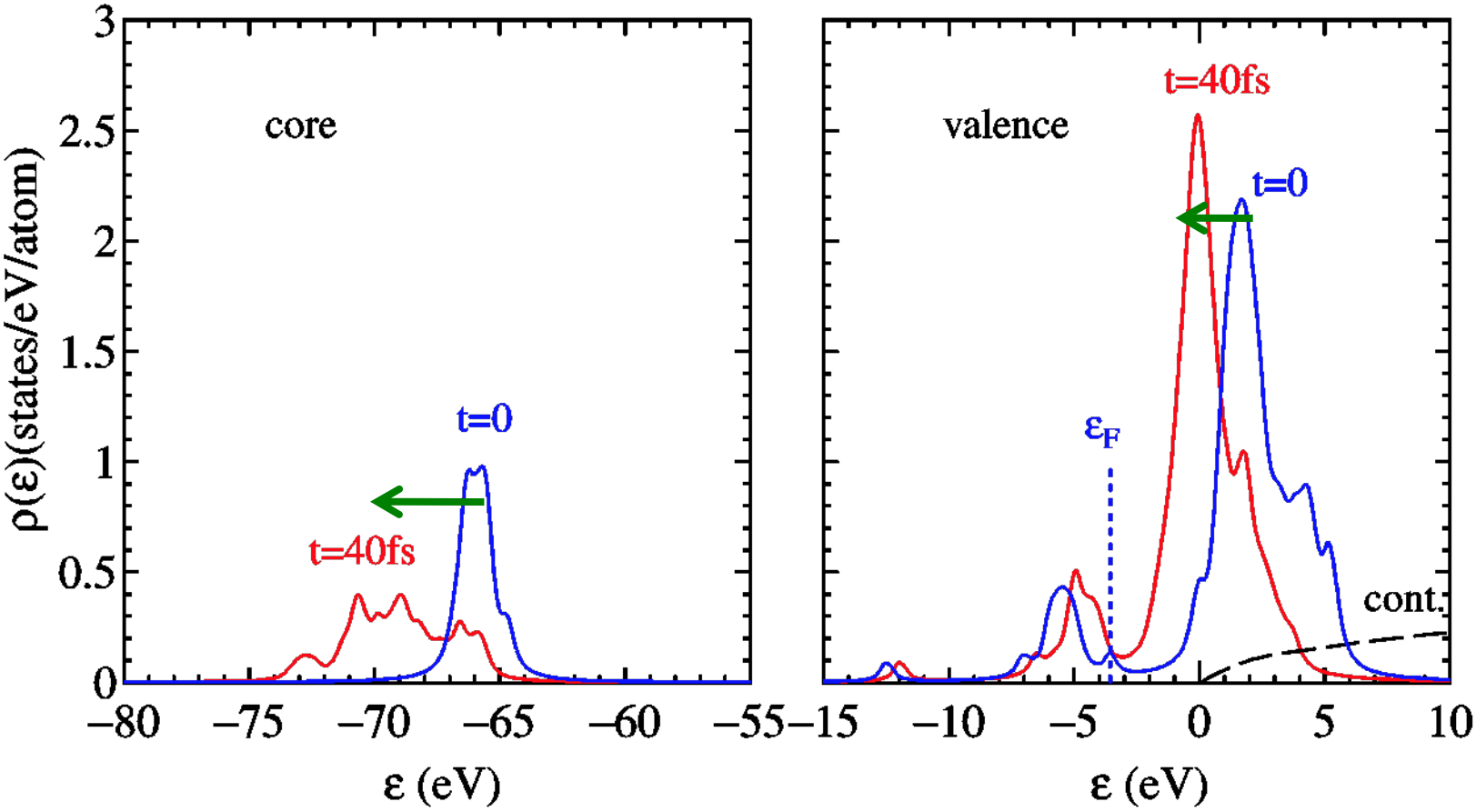


11% of core electrons excited within 40 fs

edge shift → decrease of absorption

ultrafast switch

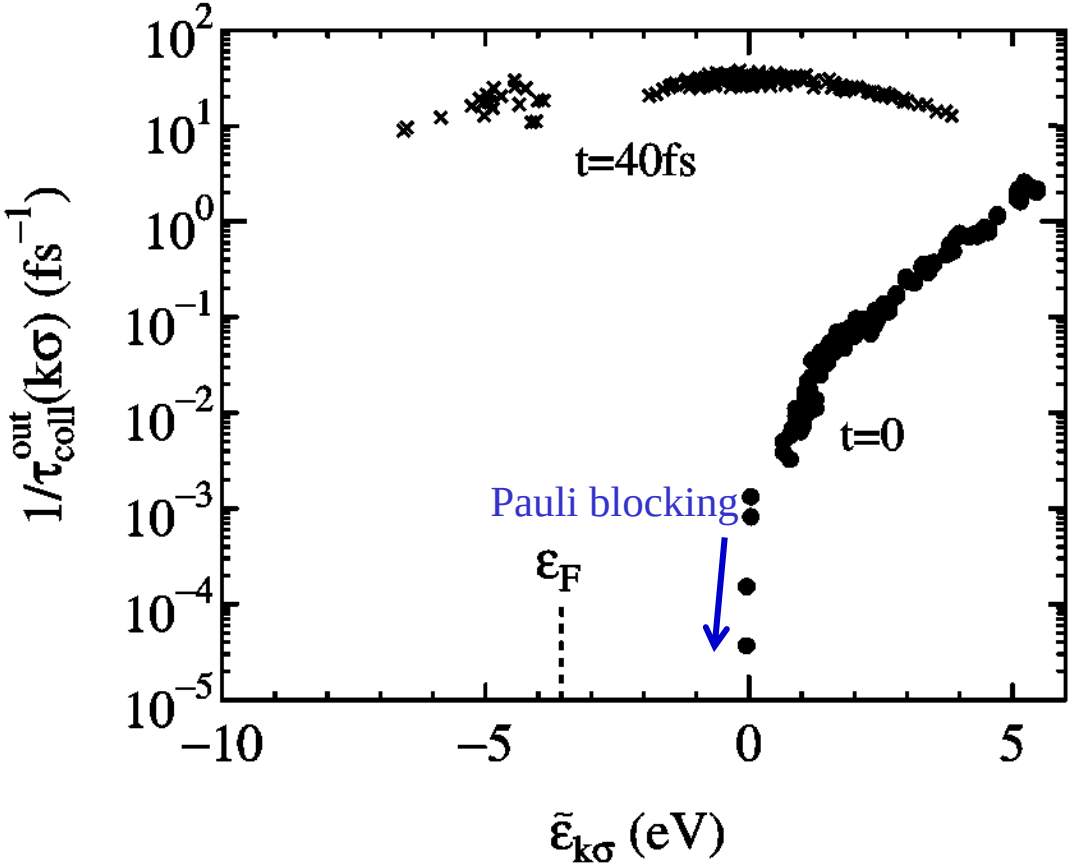
Density of states

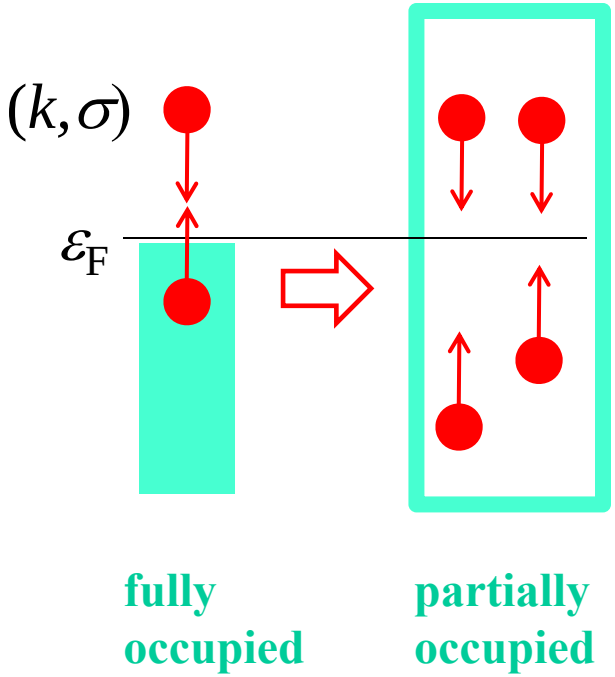


Lowering of core levels relative to the valence levels

→ blue shift of the absorption edge

Valence electron collisional relaxation rate





ground state: Pauli blocking near Fermi energy

photoexcited state → no Pauli blocking → enhanced collision rate

collision time = 0.1 fs

Summary

(1) EOS combining quantum-chemical and fluid-variational approaches

- works well for Hg critical point
- should be modified at higher temperatures (excited-state populations) and low densities (formation of molecules)

(2) QMD simulations

- can directly simulate distributions of electrons and ions
- wide applicability: various elements, high temperatures, EOS, conductivity
- difficulty: determination of critical points

(3) Photoexcitation kinetics of solids

- unrestricted Hartree-Fock + density-matrix equation of motion
- Markov approximation → collisional- radiative rate equations
- rate coefficients & energy-level shifts derived from the Hamiltonian
- difficulty: treatment of collision terms (energy conservation, screening, correlation), continuum wave functions