Modeling excess heat in the Fleischmann-Pons experiment

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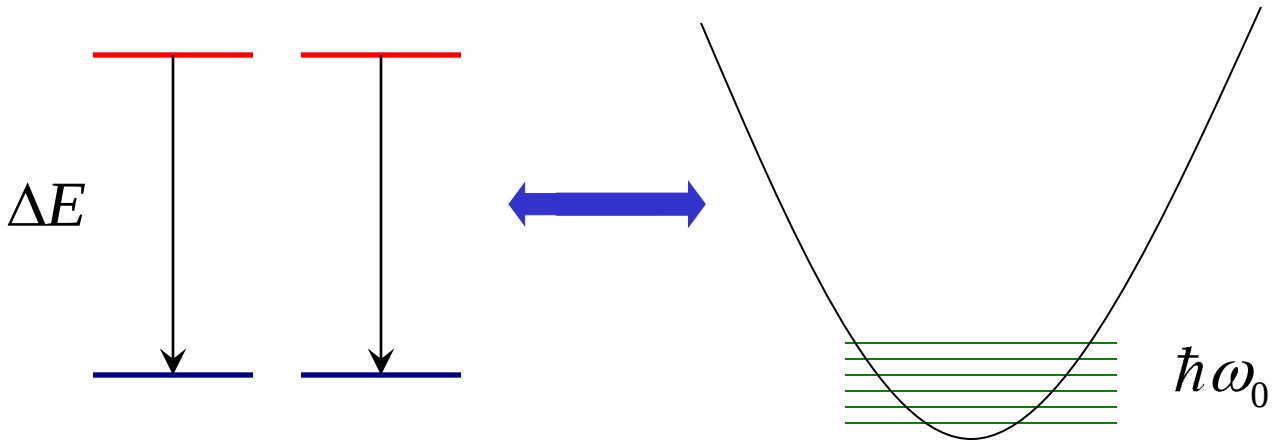
Theoretical problem

Although many more results available from experiment, we have enough so far to pose the key theory problem:

How to split up a large ΔE quantum into lots of small quanta?

The major implication of the Fleischmann-Pons experiment is that this is possible and occurs in energy production

Basic toy model



Two-level systems

Macroscopic excited mode

$$\Delta E >> \hbar\omega_0$$

Many-spin spin-boson model

C. Cohen-Tannoudji

$$\hat{H} = \Delta E \frac{\hat{S}_z}{\hbar} + \hbar\omega_0 \hat{a}\hat{a}^\dagger + V \frac{2S_x}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right)$$

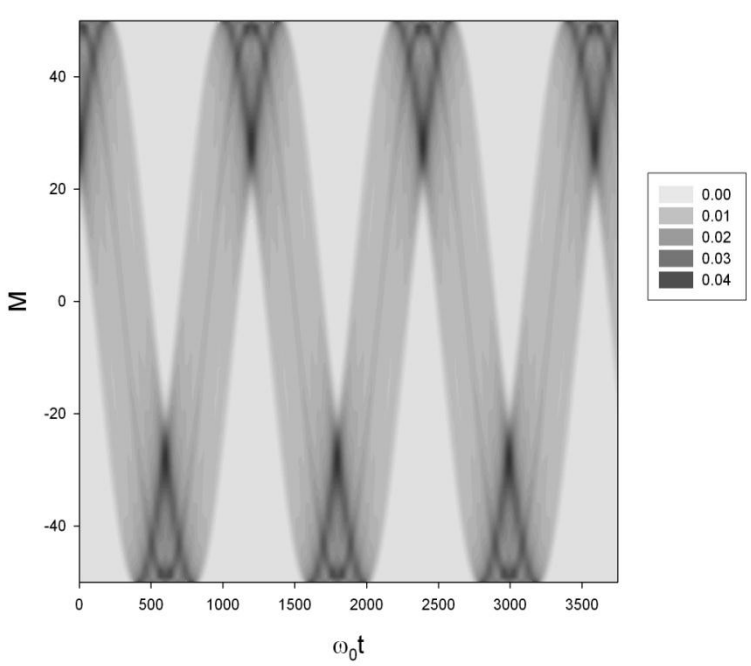
Two-level systems energy

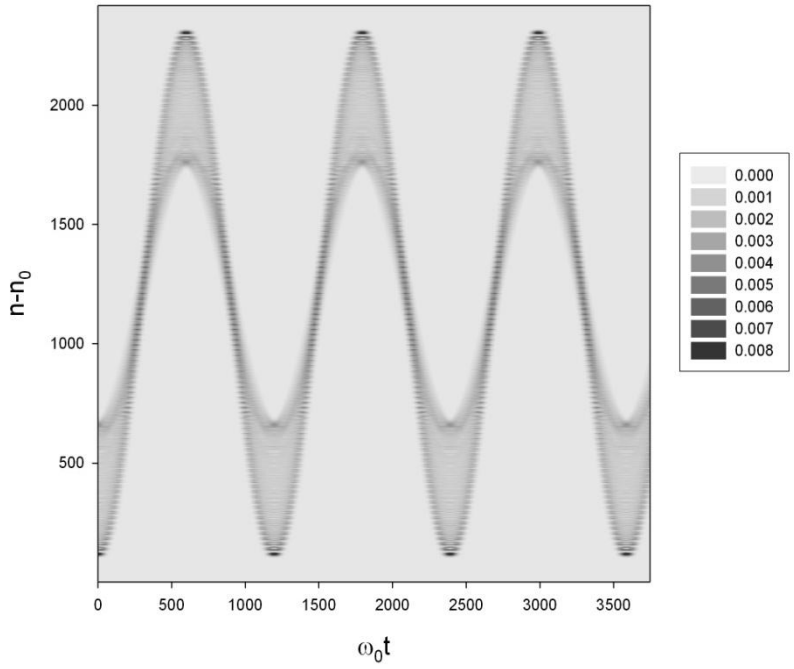
Harmonic oscillator energy

Linear coupling between two-level systems and oscillator

Earlier versions of the model due to Bloch and Siegert (1940)

Coherent energy exchange





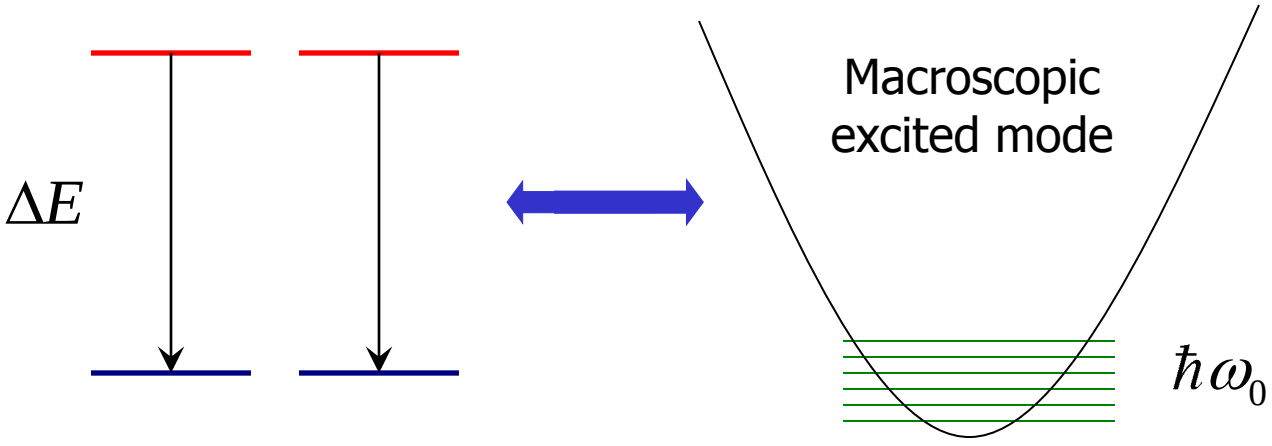
Numerical results for exchanging energy between 1700 oscillator quanta and 100 two-level systems

Thinking about toy model

Coherent multi-quantum energy exchange predicted by toy model

- Effect is weak
- Stringent resonance requirements
- Can exchange up to about 100 quanta coherently
- Exactly kind of model needed, except energy exchange effect is too weak

Improved toy model



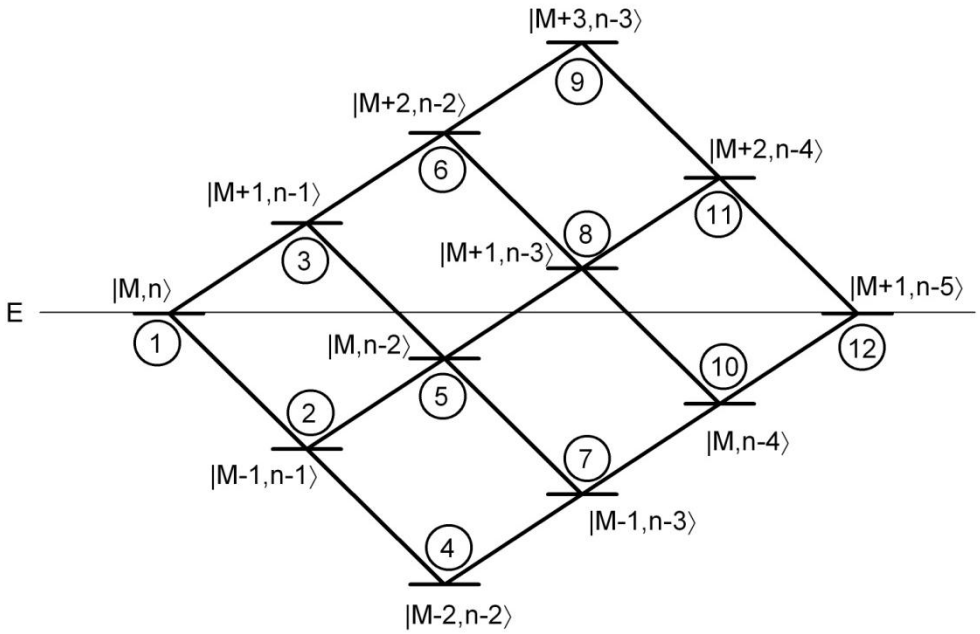
$$\Delta E \gg \hbar\omega_0$$

Lossy version of model

$$\hat{H} = \Delta E \frac{\hat{S}_z}{\hbar} + \hbar\omega_0 \hat{a}\hat{a}^\dagger + V \frac{2S_x}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right) - i\frac{\hbar}{2}\Gamma(E)$$

Loss term, which allows the system to decay when a large energy quantum is available

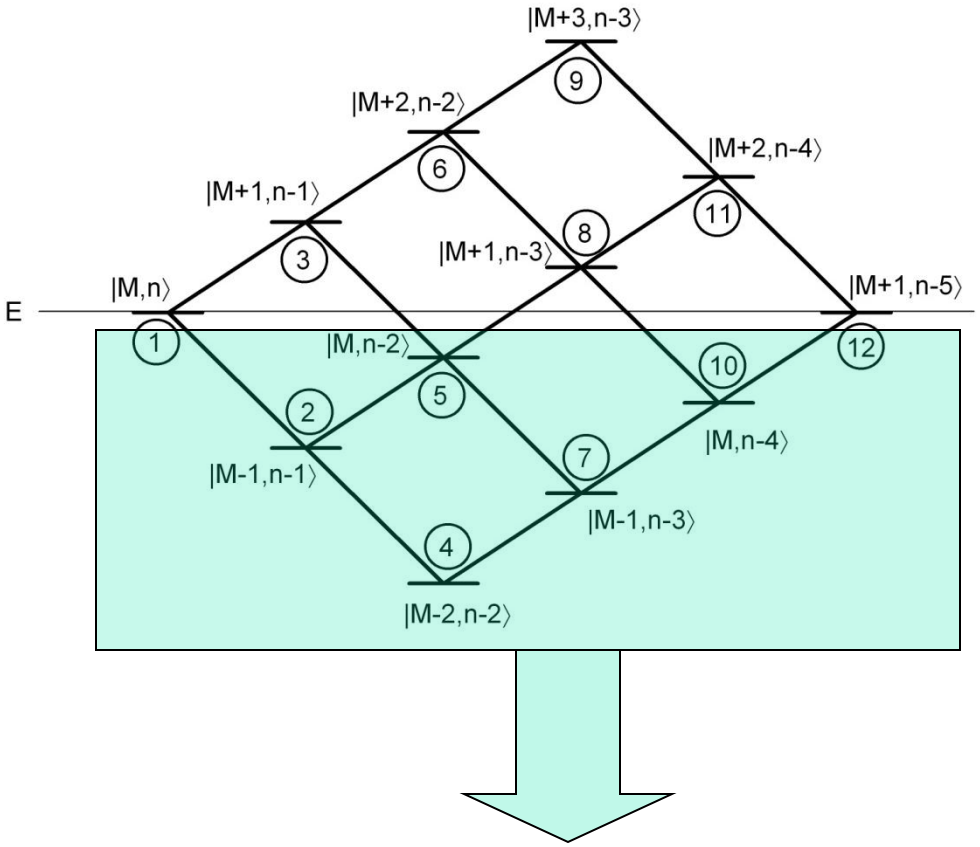
Perturbation theory



Many paths from initial to final state, with interference between upper and lower paths

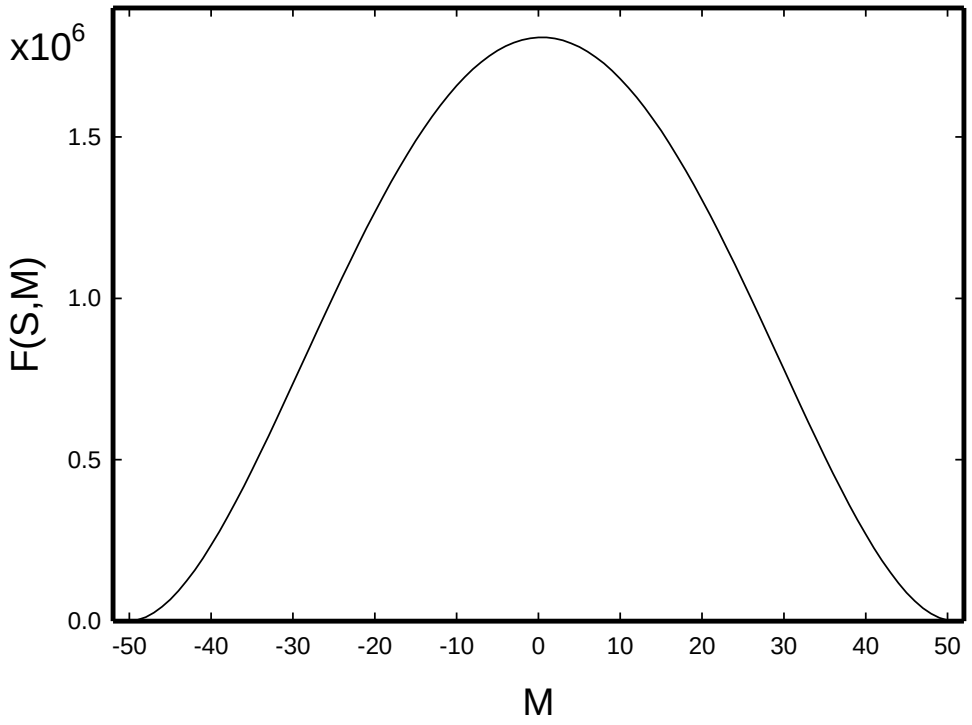
Finite basis approximation for $\left|n\right\rangle \otimes \left|M\right\rangle \rightarrow \left|n-5\right\rangle \otimes \left|M+1\right\rangle$

Perturbation theory



Loss channels available for off-resonant states with energy excess, which spoils the destructive interference

Enhancement due to loss

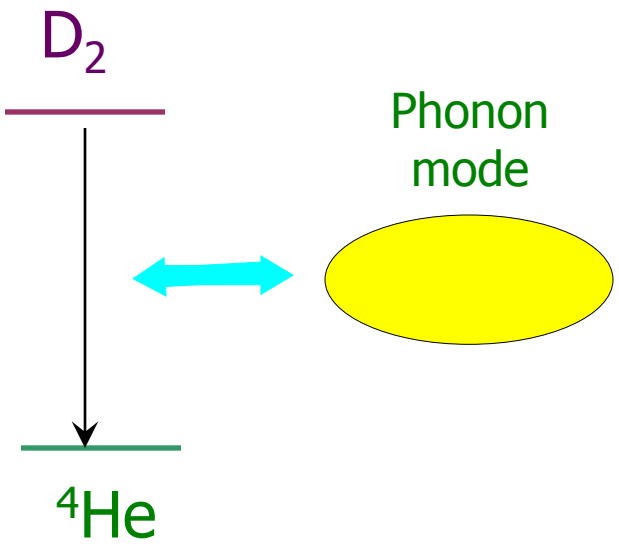


$$\left[V_{1,12}(E)\right]_{\Gamma=\infty} = \left[V_{1,12}(E)\right]_{\Gamma=0} F(S,M)$$

Lossy version of model

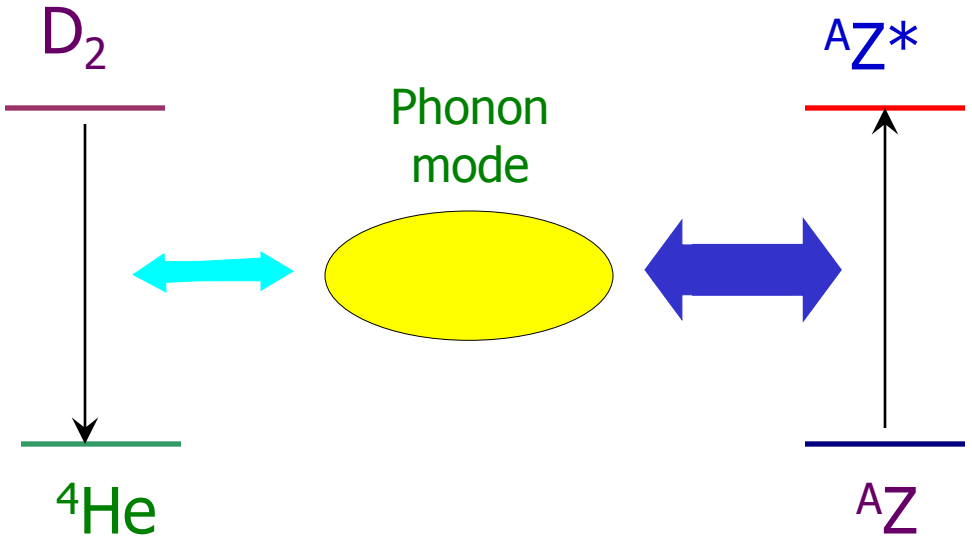
- Loss spoils the destructive interference
- Coherent energy exchange rates increased by orders of magnitude
- Much stronger effect
- Model capable of converting 24 MeV to atomic scale quanta

Thinking about PdD



Unfortunately, coupling is too weak because of Coulomb repulsion

Excitation transfer



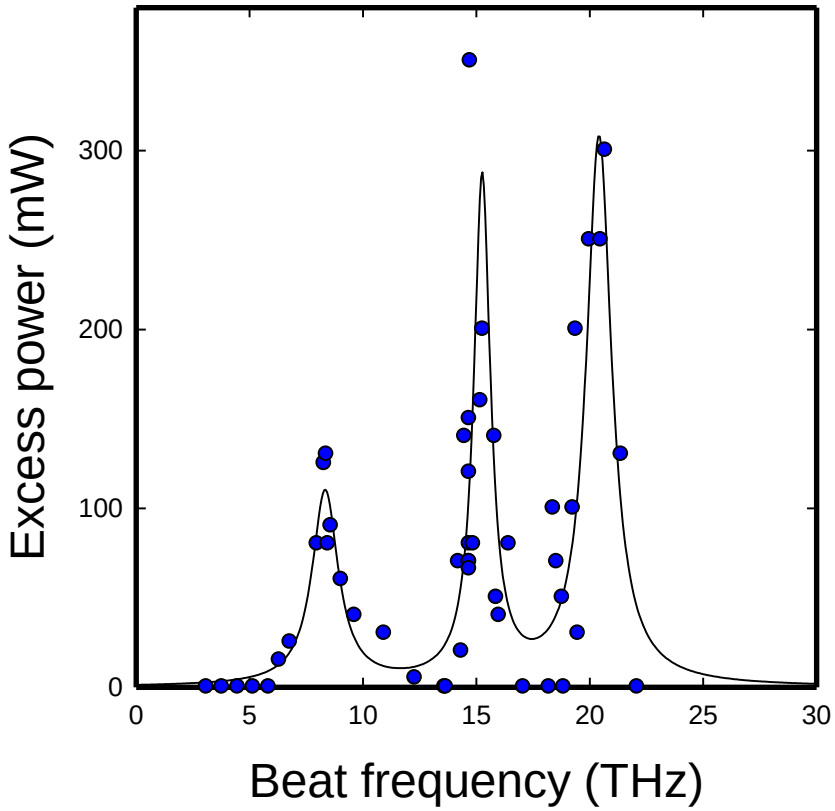
Indirect evidence from experiment implicates $^{A}Z = {}^{4}He$, and theory and experiment suggest that $^{A}Z^*$ is a localized two-deuteron state

Basic model

$$\hat{H} = \Delta E_1 \frac{\hat{S}_z^{(1)}}{\hbar} + \Delta E_2 \frac{\hat{S}_z^{(2)}}{\hbar} + \hbar\omega_0 \hat{a}\hat{a}^\dagger - i\frac{\hbar}{2}\Gamma(E)$$
$$+ V_1 e^{-G} \frac{2S_x^{(1)}}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right) + V_2 \frac{2S_x^{(2)}}{\hbar}\left(\hat{a} + \hat{a}^\dagger\right)$$

This kind of model is first one relevant to experiment

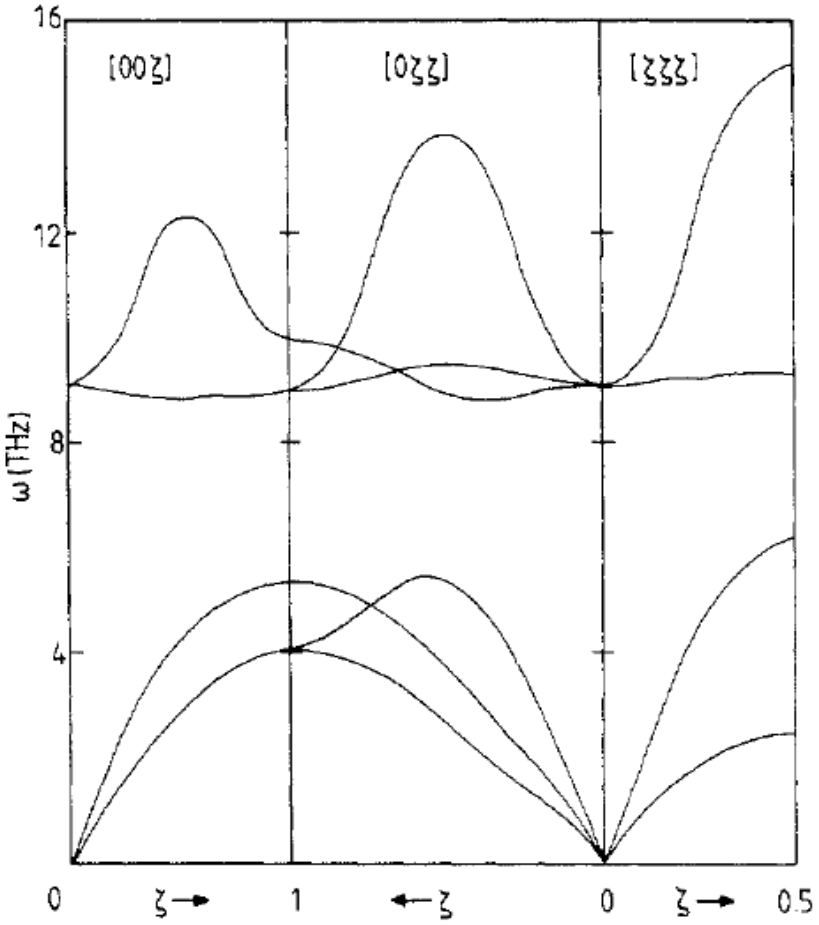
What oscillator modes?



Frequency (THz)	width (THz)
8.3	0.70
15.3	0.44
20.4	0.68

Results from dual laser experiments of Letts, *Proc. ICCF14* and *ACS Sourcebook* vol 2

Dispersion curve for PdD



L E Sansores et al
J Phys C **15** 6907 (1982)

Strong-coupling limit

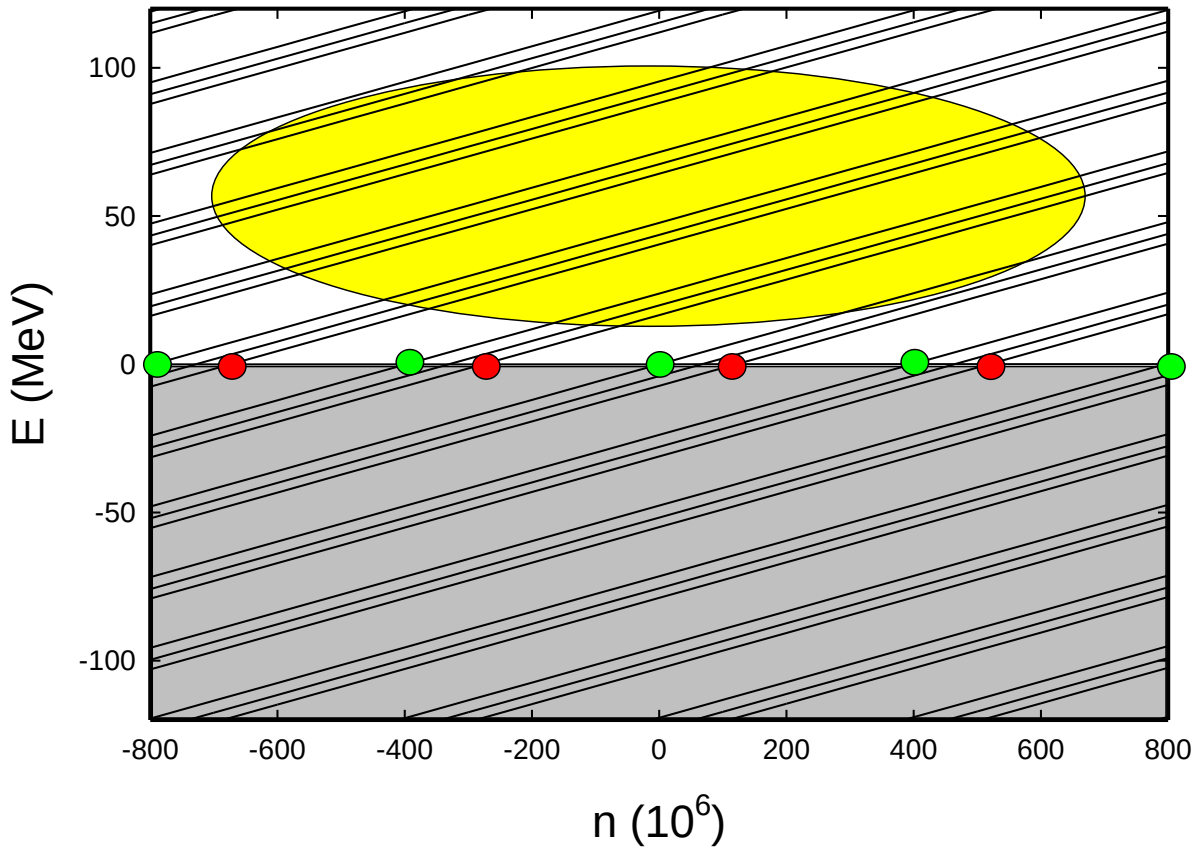
When the coupling between the receiver-side two-level systems and oscillator is strong, then the problem simplifies

$$\Gamma \rightarrow \frac{\hbar\omega_0}{\Delta E(g)}\left|\frac{\langle S, M, n+\Delta n|\hat{H}|S, M+1, n\rangle}{\hbar}\right|$$

When the excitation transfer step is the bottleneck, then

$$\Gamma = \frac{V_1\sqrt{n}}{\hbar}\left(\frac{\hbar\omega_0}{\Delta E}\right)e^{-G}\sqrt{(S+M)(S-M)}$$

Occupation of virtual levels



Conclusions so far

- Can model the effect
- Can see the energy exchange with the lattice
- Can see excitation transfer
- Can get rates for both
- Agreement with experiment if screening energy U_e = 150 eV

Trying out simplified version

$$\frac{d}{dt}N_{D2} + \frac{N_{D2} - N_{D2}^{0}}{\tau_{D2}} = -\Gamma_0 \sqrt{N_{D2} N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

$$\frac{d}{dt}N_{He} + \frac{N_{He} - N_{He}^{0}}{\tau_{He}} = \Gamma_0 \sqrt{N_{D2} N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

$$\frac{d}{dt}n + \frac{n - n_0}{\tau_p} = \gamma_J + \frac{\Delta E}{\hbar\omega_0}\Gamma_0 \sqrt{N_{D2} N_{He}}\,\Theta\left(n - n_{thresh}\right)$$

Example: fast He diffusion

Active region:
$A = 1\ cm^2$
$\Delta r = 100\ nm$

D_2 parameters:
f[vacancy] = 0.25
$f[D_2] = 0.005$
$N[D_2] = 1.8 \times 10^{15}$
$\tau_{D2} = 2 \times 10^{-8}$ sec

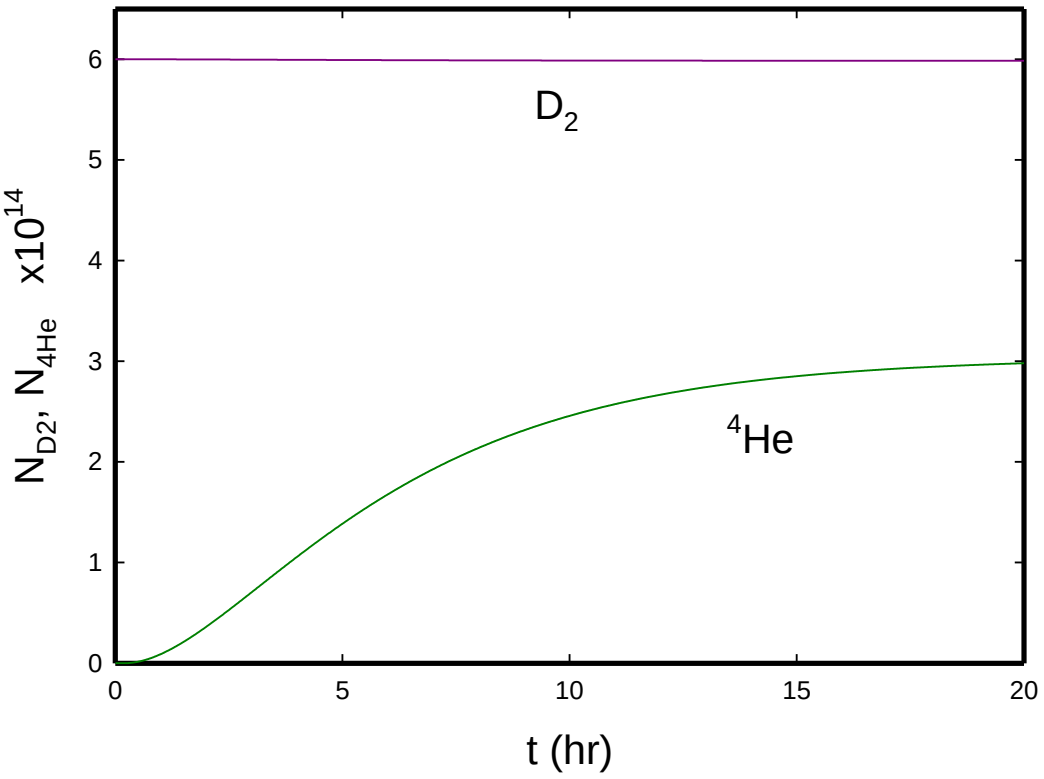
^{4}He parameters:
$D_{He} = 1.3 \times 10^{-14}\ cm^2/sec$
$\tau_{He} = \Delta r^2/D_{He} = 2.1$ hr

Phonon mode:
$f_0 = 8.3$ THz
Q = 20

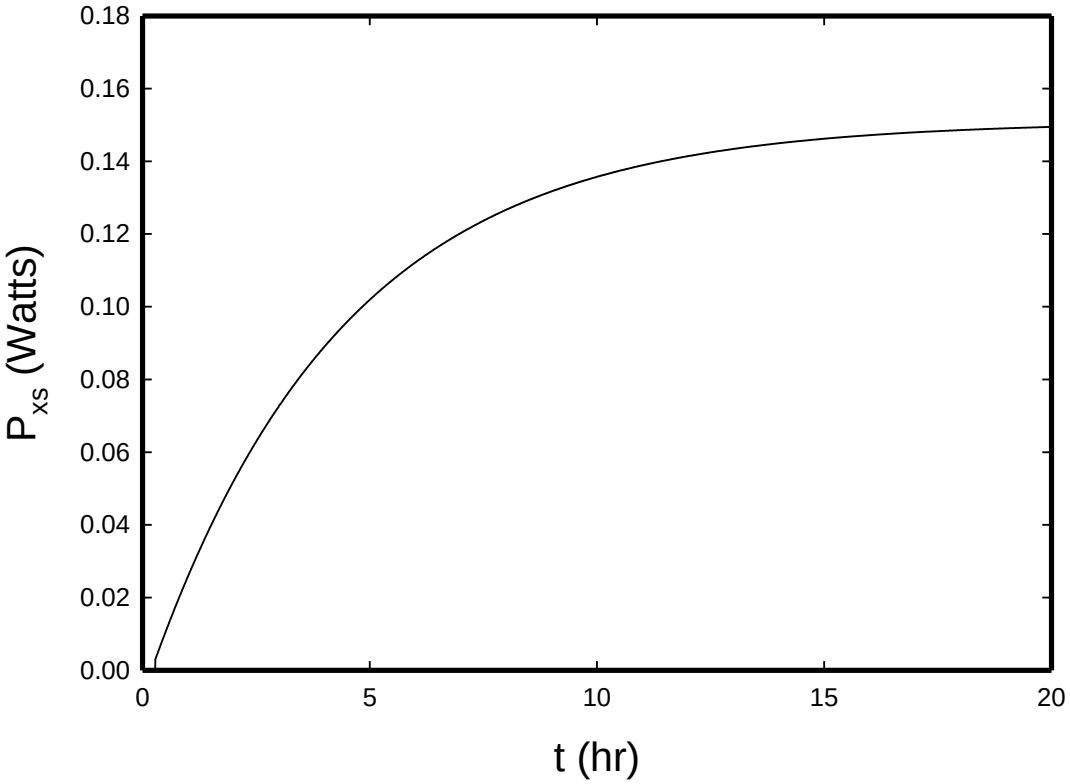
Deuterium flux:
$P_{flux} = 1\ Watt/cm^3$
$n_{thresh} = 100$

Basic reaction rate:
$\Gamma_0 = 1/(3\ hr)$

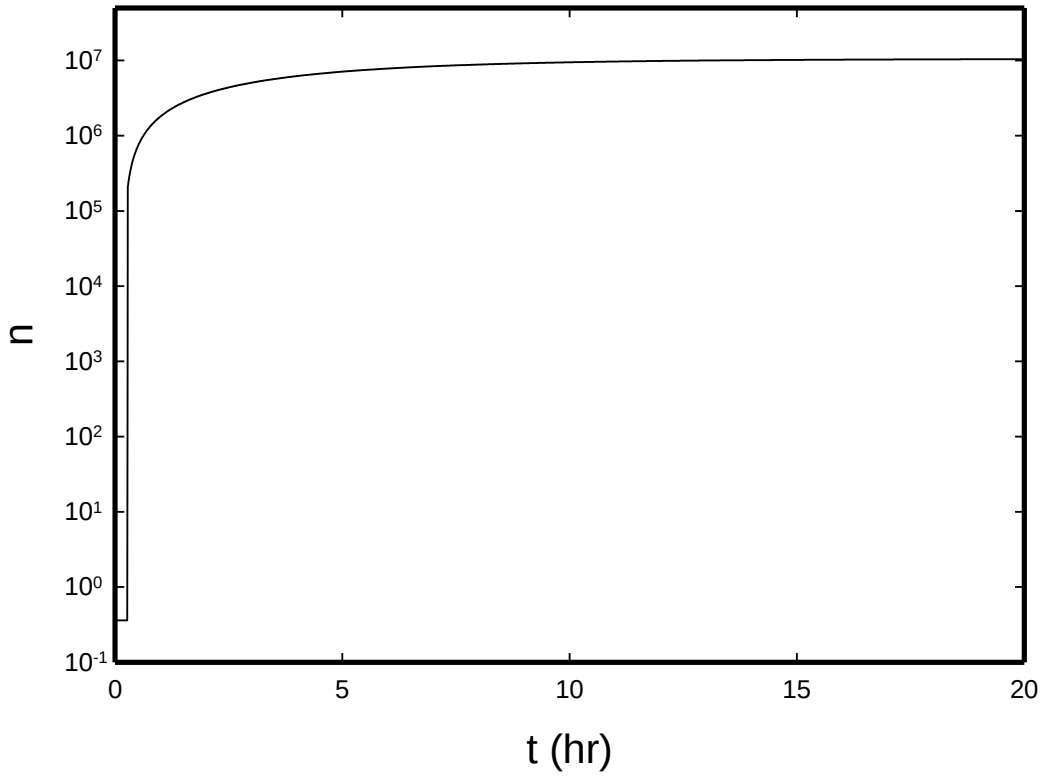
Evolution of dideuterium, ^4He



Excess power



Number of phonons



Thermal: 0.36 Flux generated (1 W/cm^3): 700 P_{xs} generated: 10^7

Addressing the full problem

Start out with full problem

$$E\Psi = H\Psi$$

Then implement picture and approximation through construction of channels

$$\Psi = \sum_j \psi_j \Phi_j$$

Get coupled-channel equations

$$\langle \Phi_i | E\Psi = \langle \Phi_i | H\Psi$$

Coupled-channel equations

Coupled-channel equations that result

$$E\psi_i = H_{ii}\psi_i + \sum_{j \neq i} H_{ij}\psi_j$$

Can put whatever physics that one likes into the channels.
Best place to start is with

$$H = H[\text{nucleons}] + H[\text{electrons}] + V[\text{strong force}] + V[\text{Coulomb}]$$

Coupling

Terms that couple from one channel to another:

$$H_{ij} = \left\langle \Phi_i \middle| H \middle| \Phi_j \right\rangle$$

We focus on strong force terms, although others present

$$H_{ij} = V_n e^{-iS_D}$$

Strong force

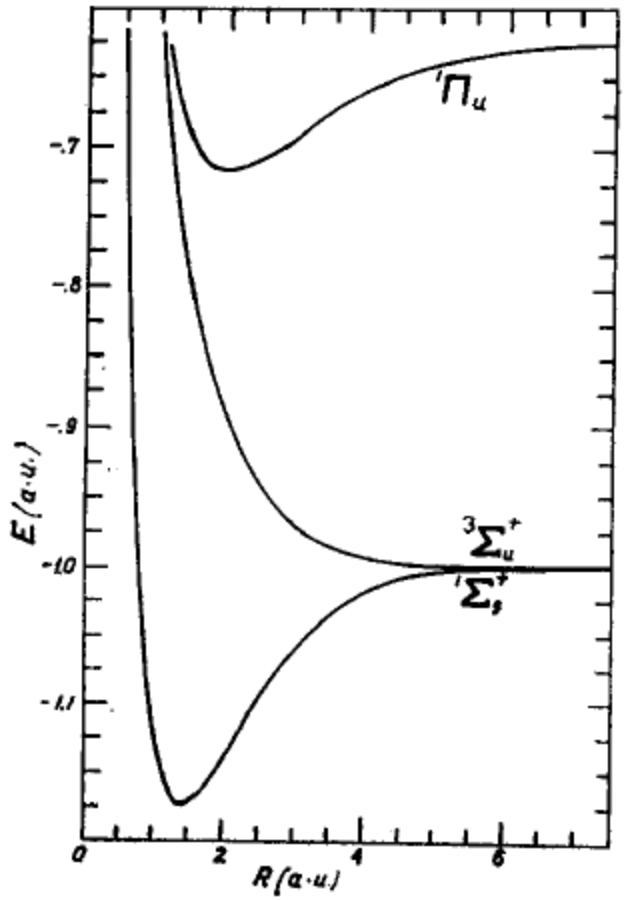
Lattice change

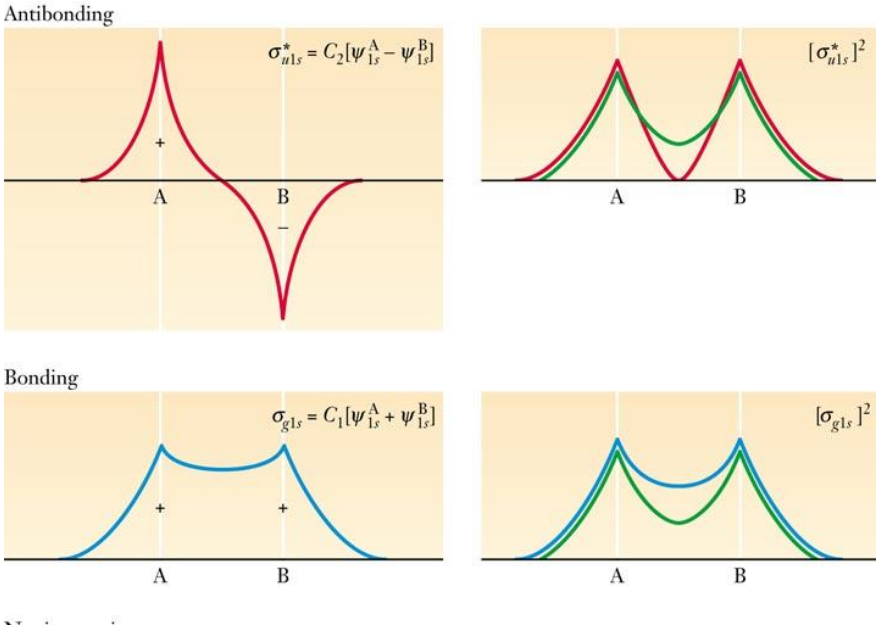
Where is the D_2?

Molecular D_2 does not form in bulk PdD

- Issue is electron density
- Computation of D_2 in electron gas leads to occupation of antibonding states
- The electron density in PdD is too high
- If you want D_2, you have to lower the electron density

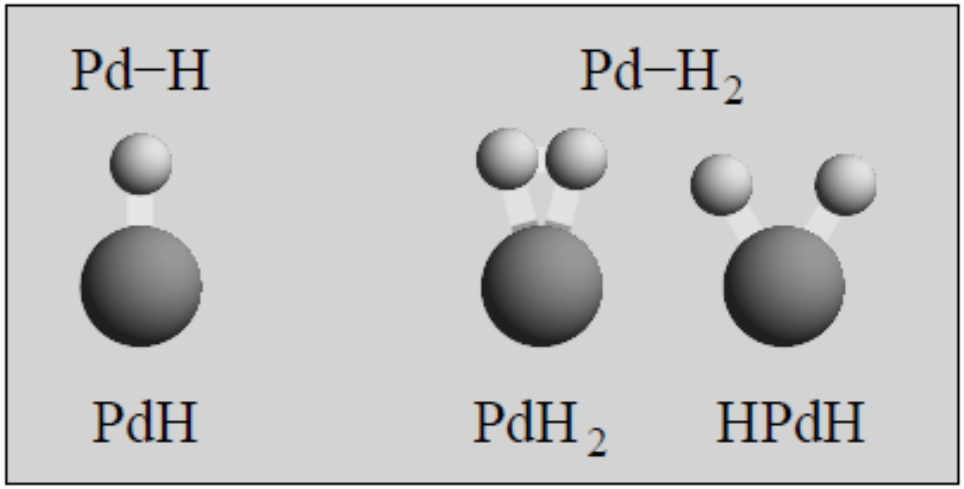
Bonding and anti-bonding in H_2





W. Kolos and L. Wolniewicz,
J Chem Phys **43** 2429 (1965)

Pd-H_2 with σ-bonding



In Pd-H_2

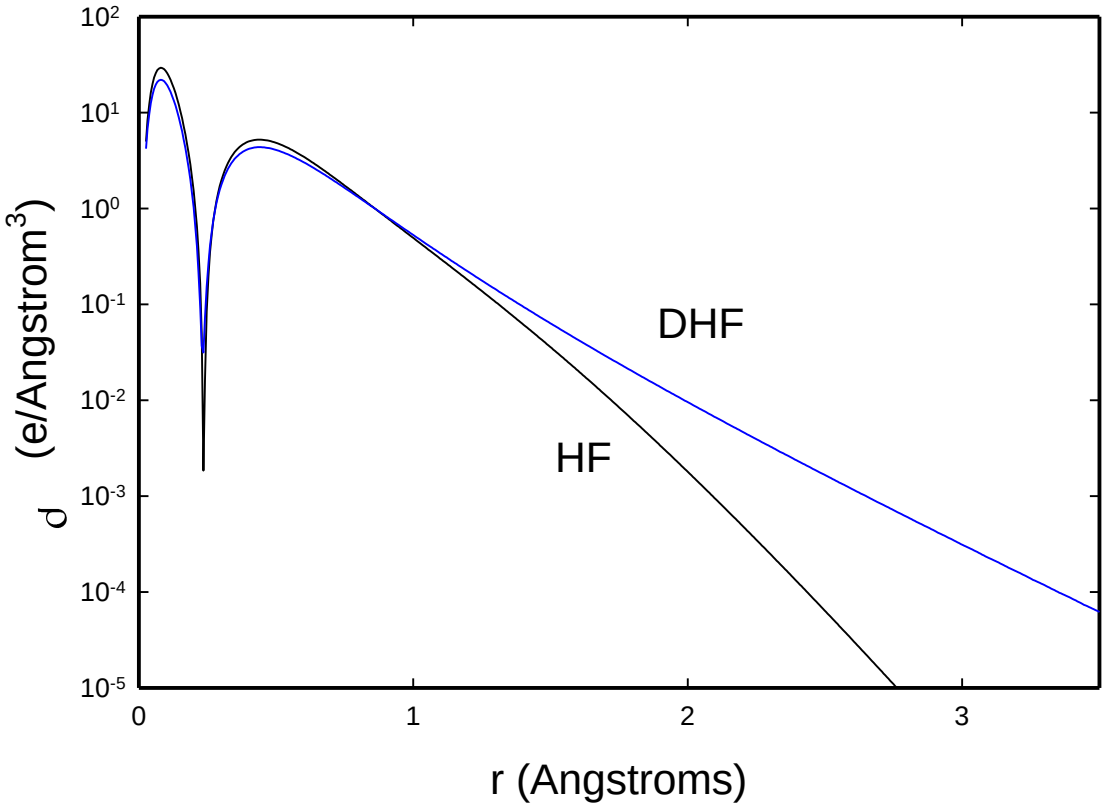
d[Pd-H]=1.67 A

d[H-H] = 0.81 A

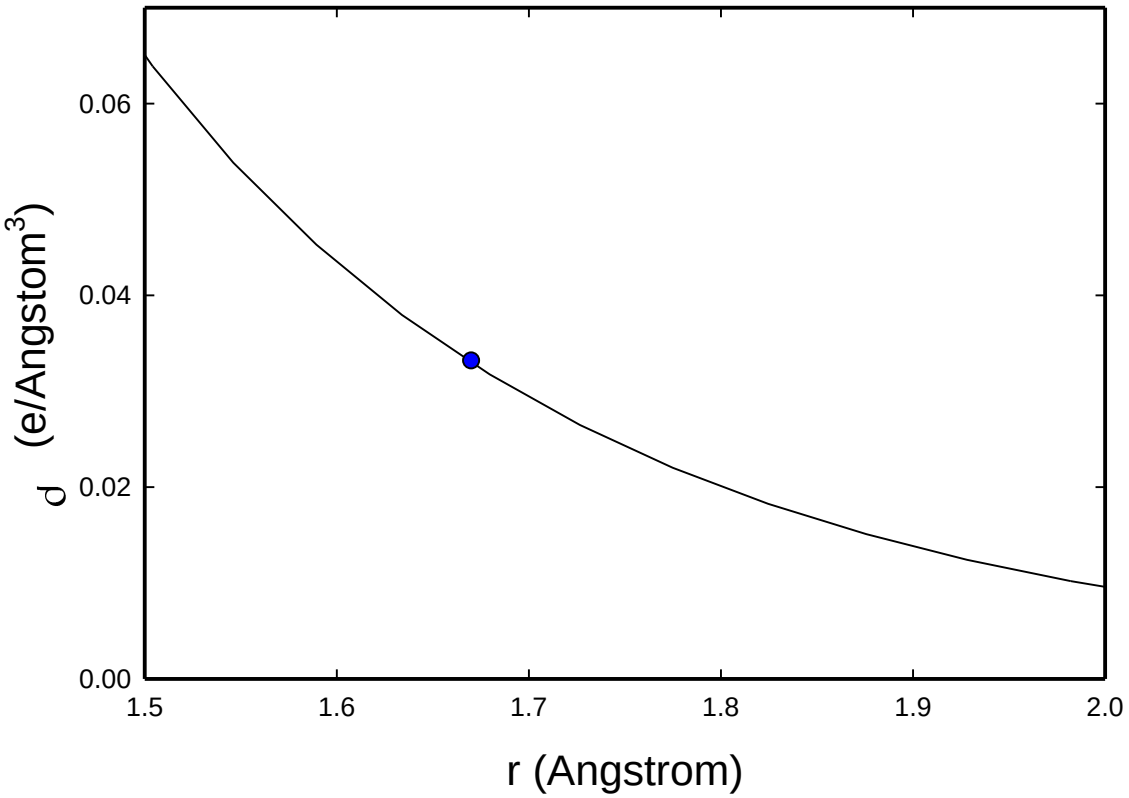
σ-bonded Pd-H_2 is the ground state of the three-atom system.

It is a combination of $(4d)^{10}\ {}^1S_0$ Pd and $(1\sigma)^2\ {}^1S_0$ H_2

Electron density of Pd $(4d)^{10}$

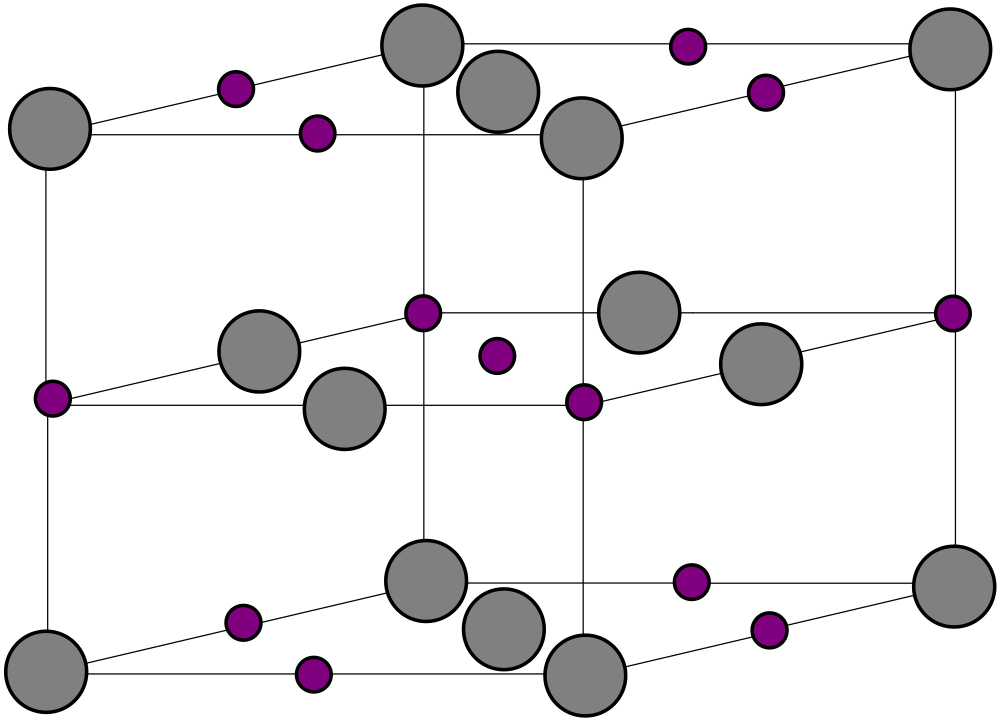


Electron density at Pd-H distance

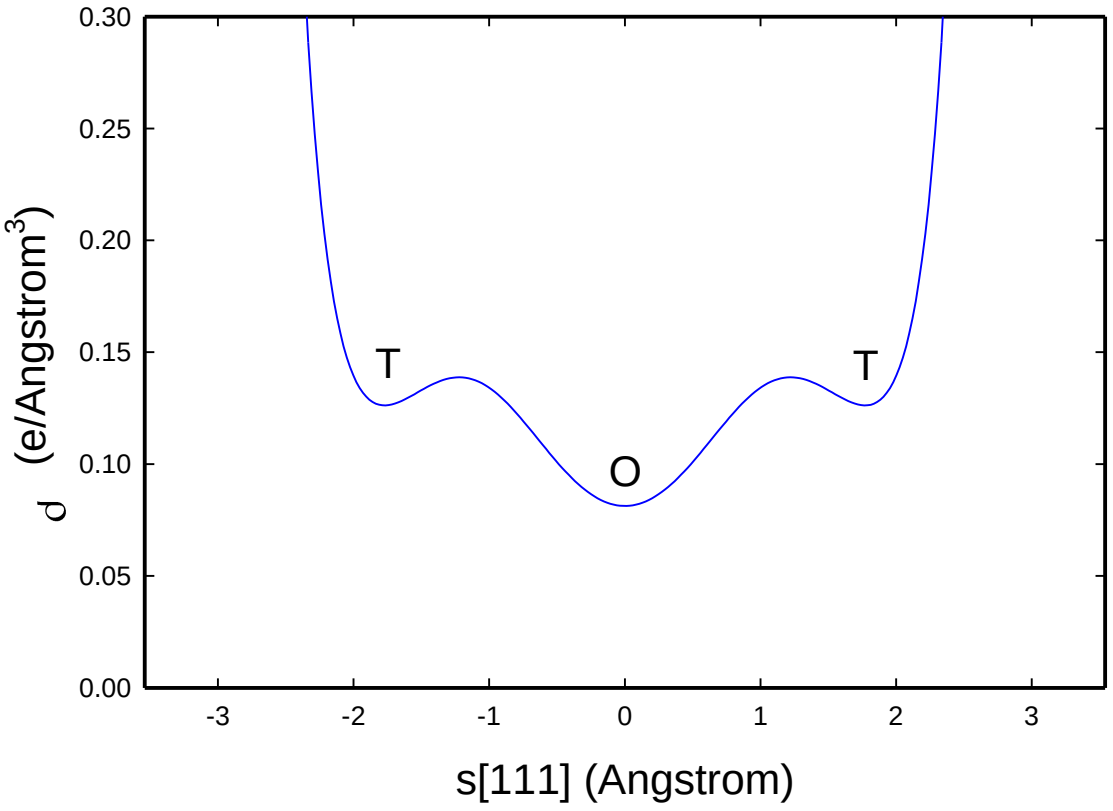


Pd-H distance in Pd-H_2 is 1.67 Angstroms, and electron density is 0.033

PdD lattice structure (fcc)



Electron density due to Pd around octahedral site



Cannot form D_2 at O-site

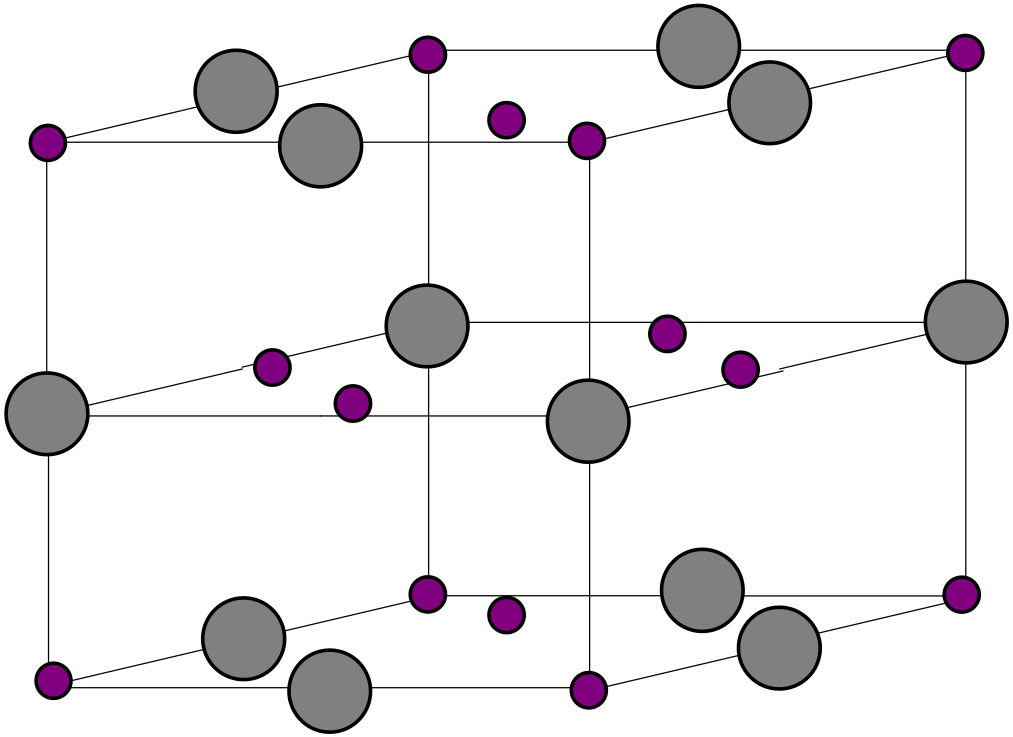
H_2 binds with Pd at 1.67 Angstroms Pd-H separation

Electron density at 1.67 Angstroms is 0.33 e/Angstrom^3

Electron density at O-site in PdD is 0.081 e/Angstrom^3

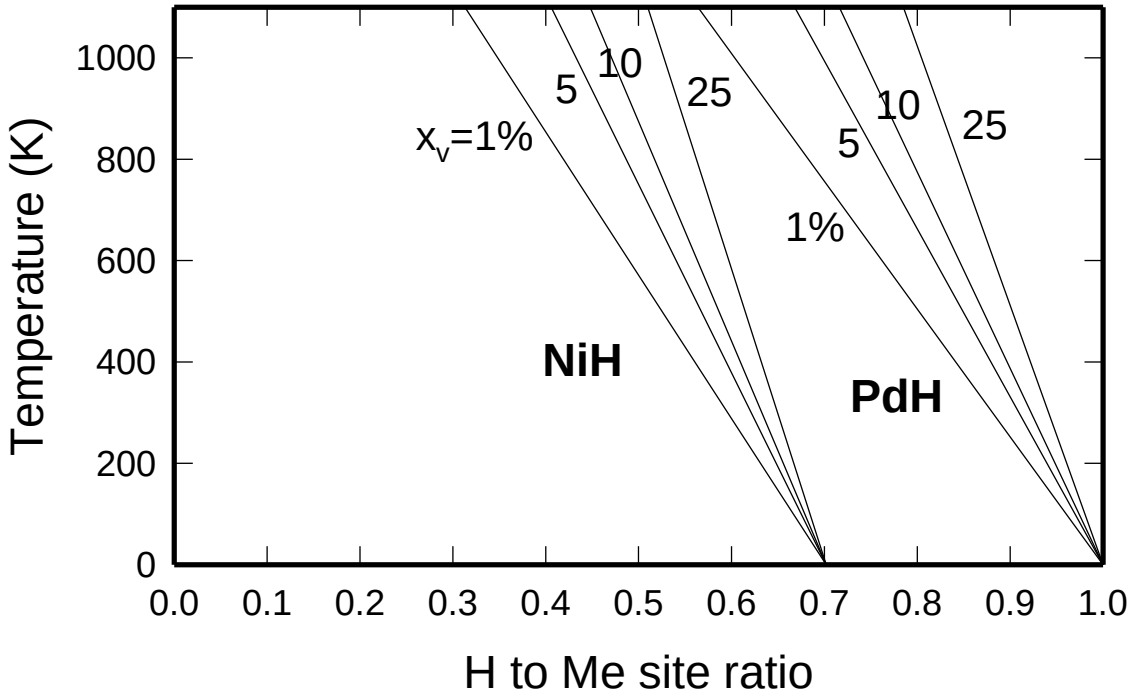
Anti-bonding orbitals occupied

PdD Host lattice vacancy



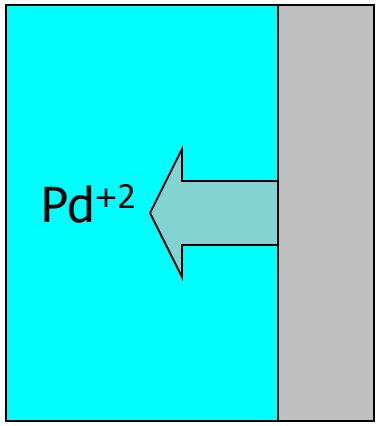
Deuterium atoms relax toward host vacancy

Vacancies in host lattice

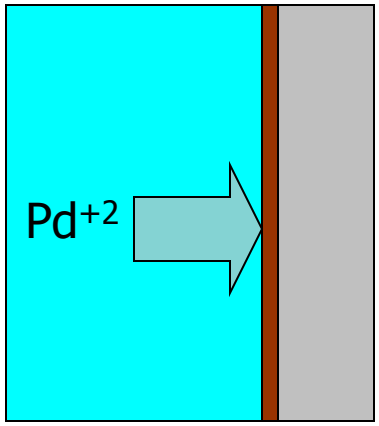


Vacancies in host metal lattice are thermodynamically favored at high loading

Codeposition



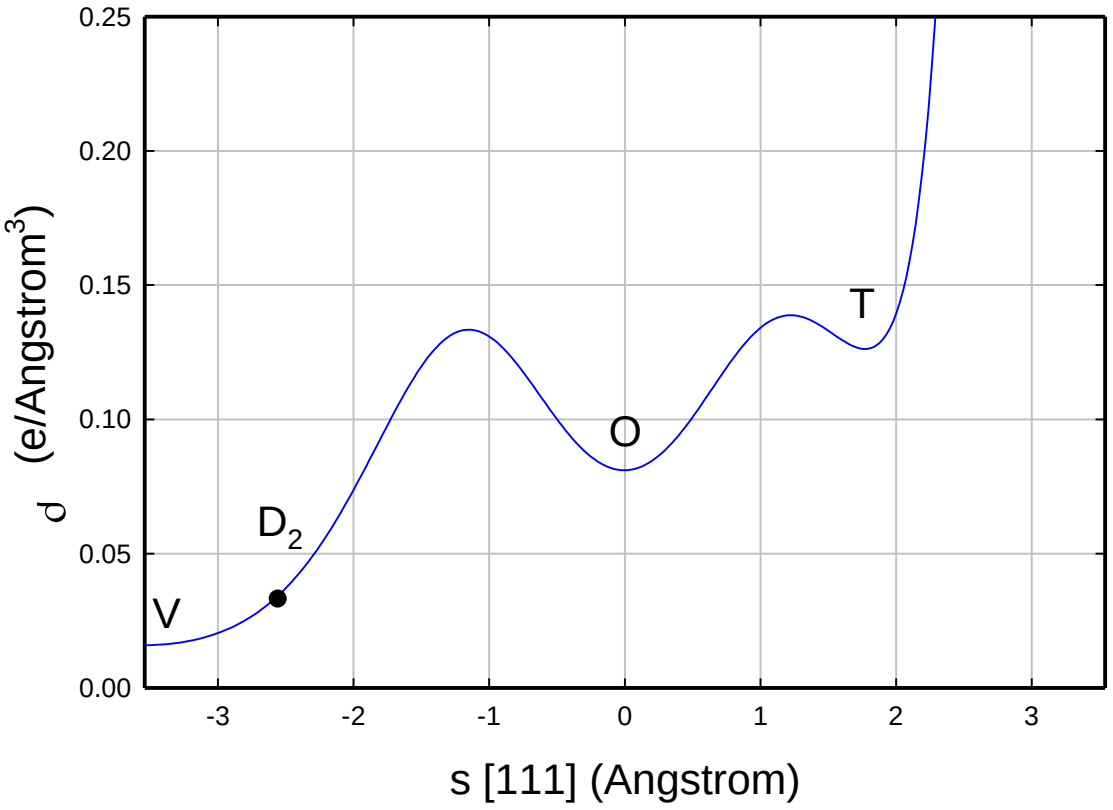
Anodic current



Cathodic current

Conjecture that a small amount of Pd is stripped off during anodic current cycles, and then codeposited during subsequent cathodic loading [most of the Pd in solution is $Pd(OH)_4^{-2}$, Mountain and Wood (1988)]

Electron density with vacancy

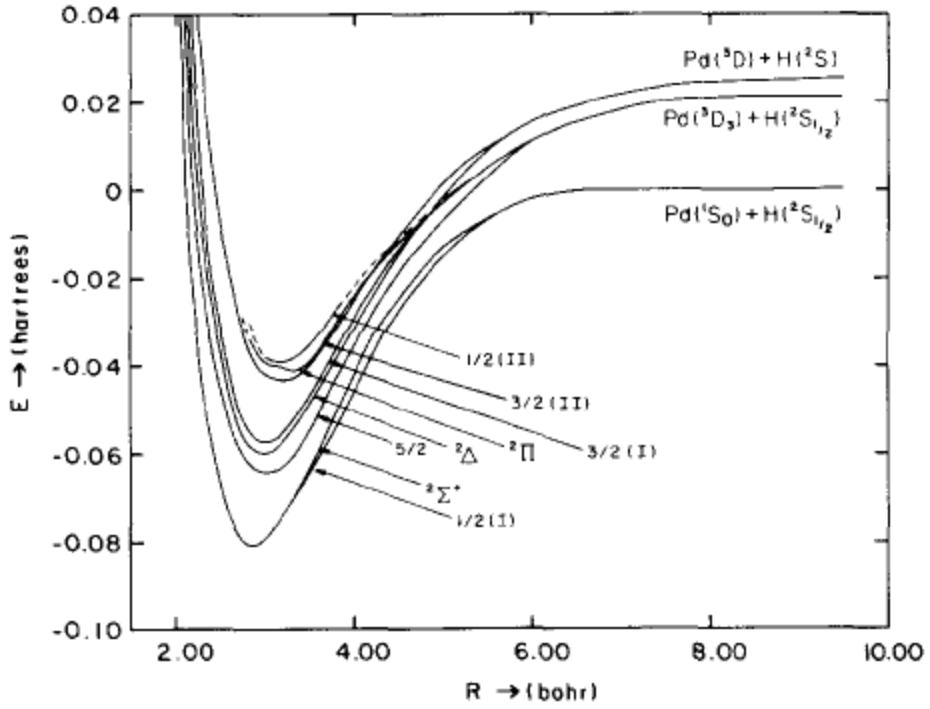


Electron density seems low enough

Superposition of atomic electron densities leads to a model electron density of 0.016 e/Angstrom^3

- Model electron density is 2x lower than for Pd-H_2
- Would expect D_2 formation near vacancy
- Would expect relevant literature

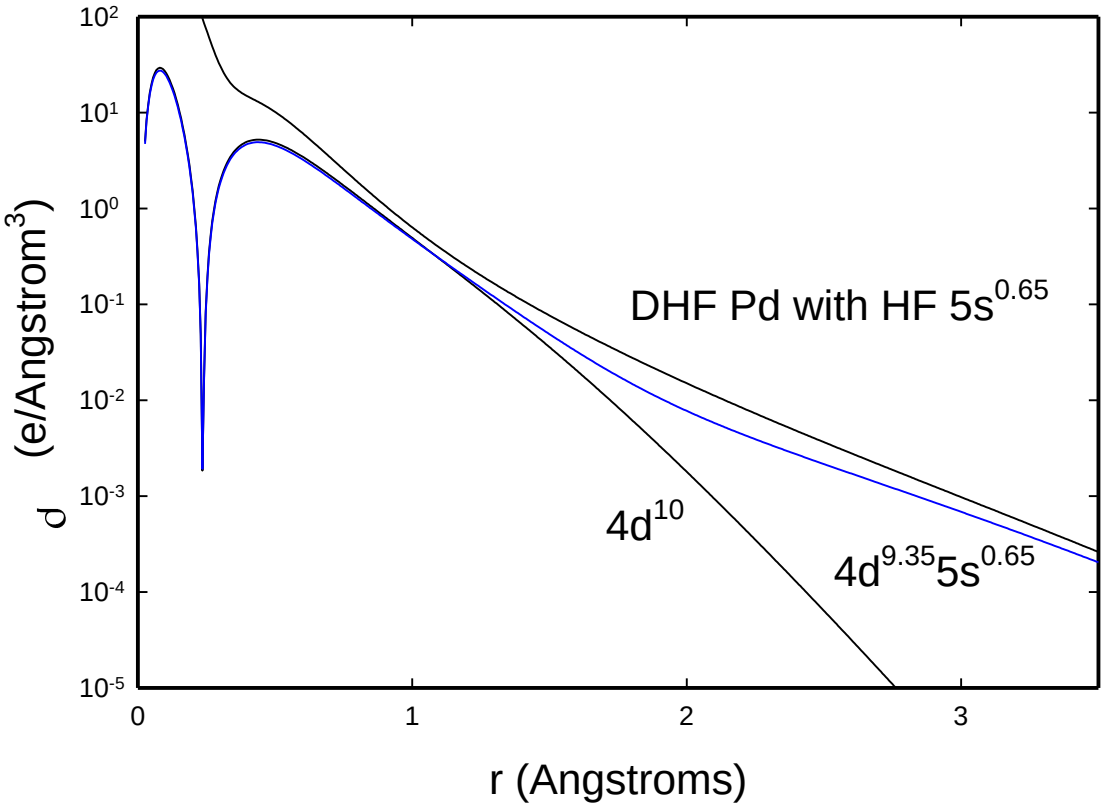
Check with PdH



For ground state
d[Pd-H] = 1.53 A

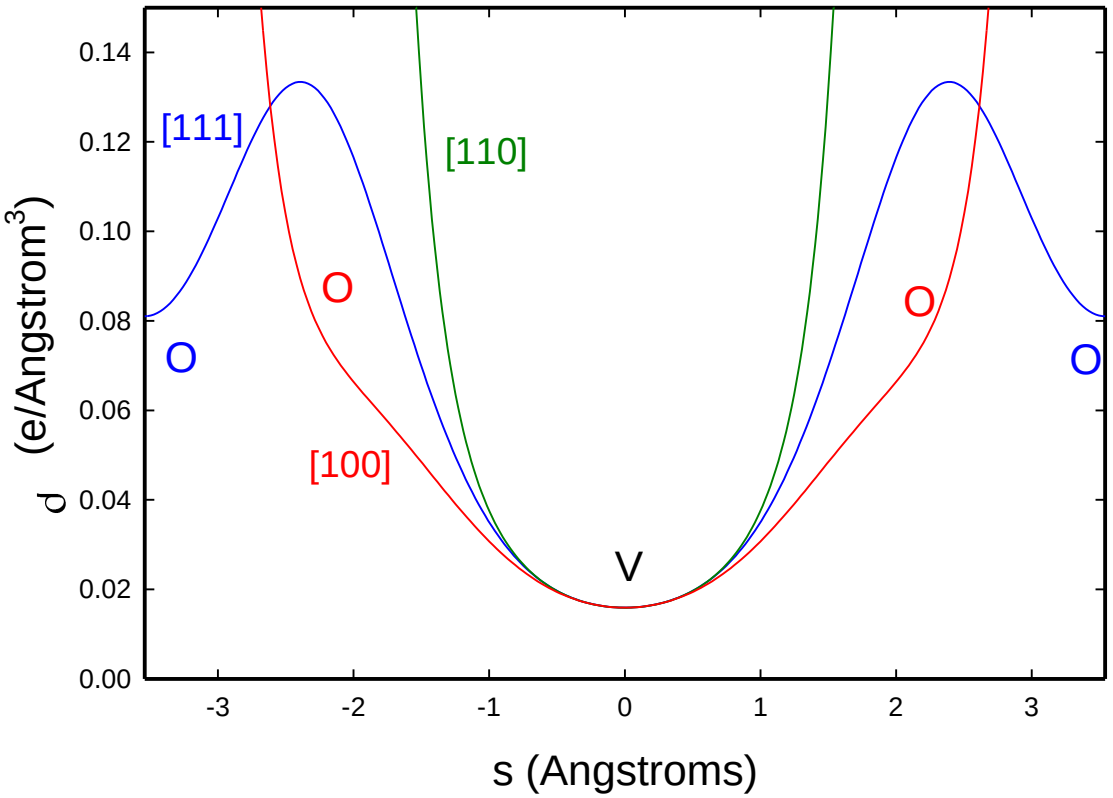
K. Balasubramanian et al, *J Chem Phys* **87** 3981 (1987)

Look at Pd density at 1.53 A



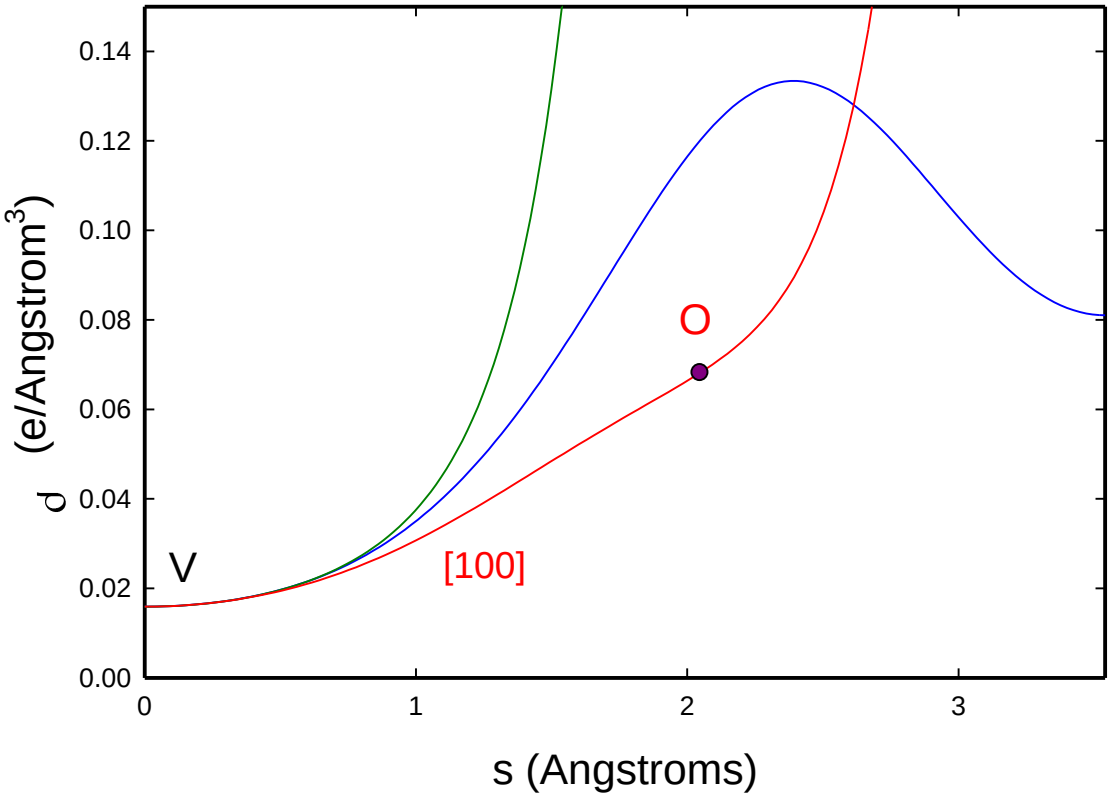
Model electron density at 1.53 A is 0.0686 e/Angstrom^3

Electron density around vacancy

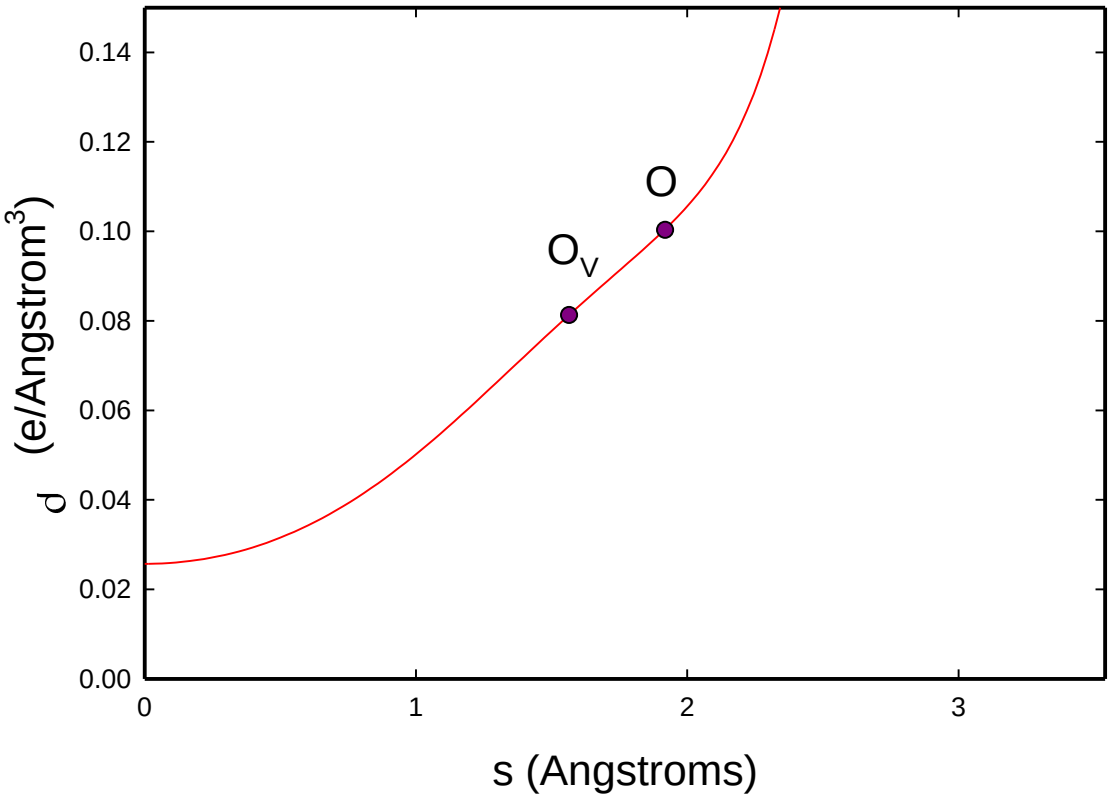


Nearest O-point no longer a minimum in electron density

Model electron density just right now for H



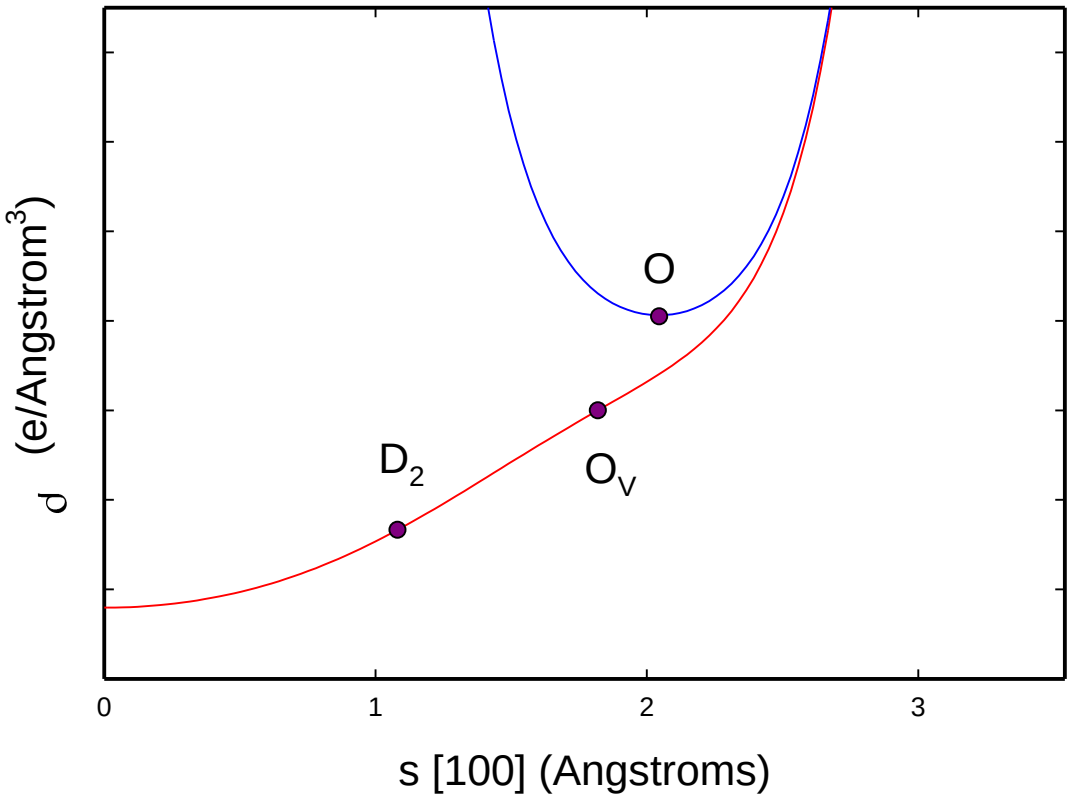
Compare with Velikova et al (2009) DFT for Pd



Velikova et al, *Phys Rev B* **80** 024101 (2009)

Velikova shift corresponds to 0.081 e/Angstrom^3 , close to PdH 0.069 e/Angstrom^3

Summary (need VASP calculation!)



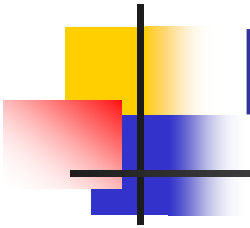
Expect about 0.4 A shift of D, and about 1 A shift for D_2 location

Summary and conclusions

- Fleischmann-Pons experiment points to new kind of physical process where nuclear energy generated with no energetic reaction products

- Spin-boson model provides analog which can convert a big quantum to a large number of small quanta, but effect is weak

- Lossy spin-boson model can convert a large number a big quantum to a large number of small quanta, and effect is large



More conclusions

- We can construct coupled-channel equations systematically to implement lossy spin-boson type scheme in real physical system

- Detailed modeling now under way