



# Modeling excess heat in the Fleischmann-Pons experiment

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# Theoretical problem

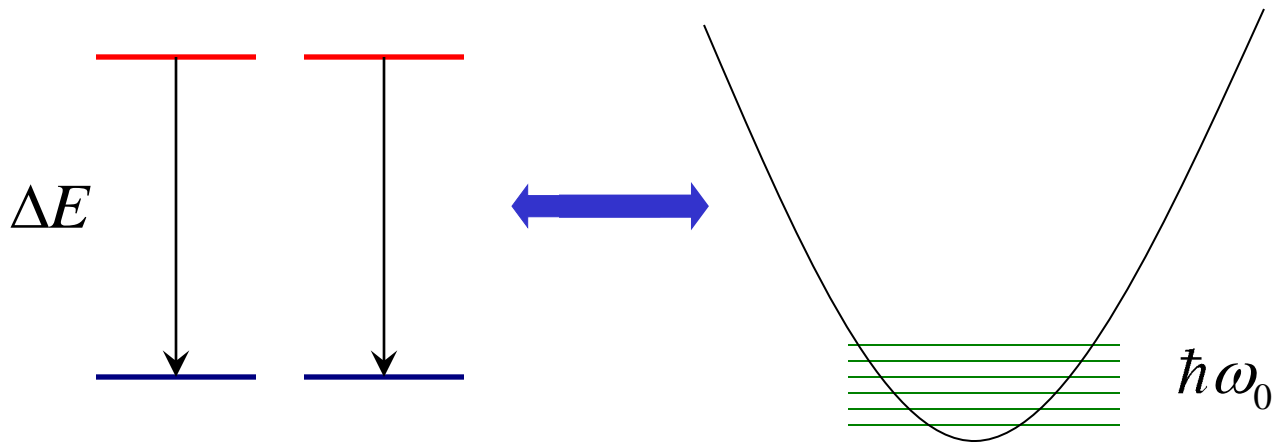
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Although many more results available from experiment, we have enough so far to pose the key theory problem:

How to split up a large  $\Delta E$  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

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

# Many-spin spin-boson model



C. Cohen-Tannoudji

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

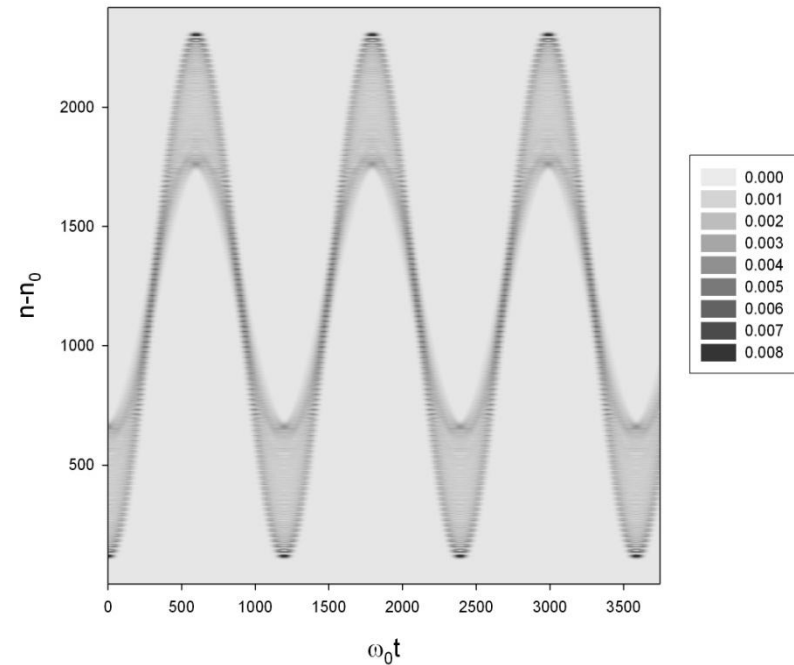
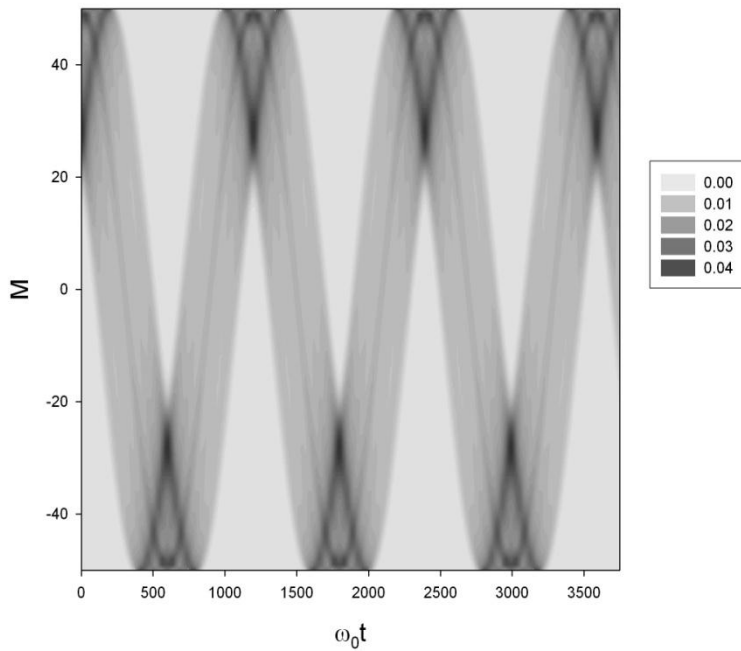
Two-level systems  
energy

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



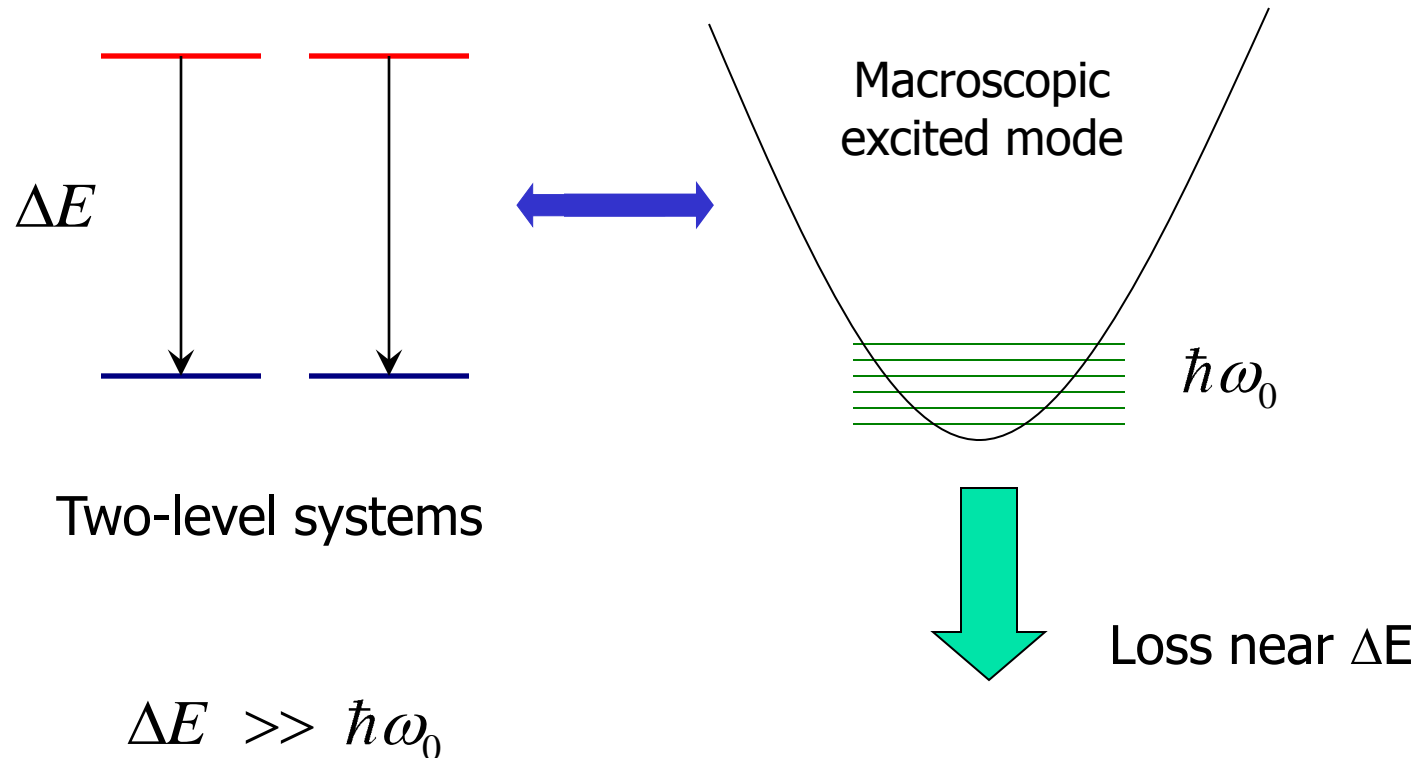
# Thinking about toy model

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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






# Lossy version of model

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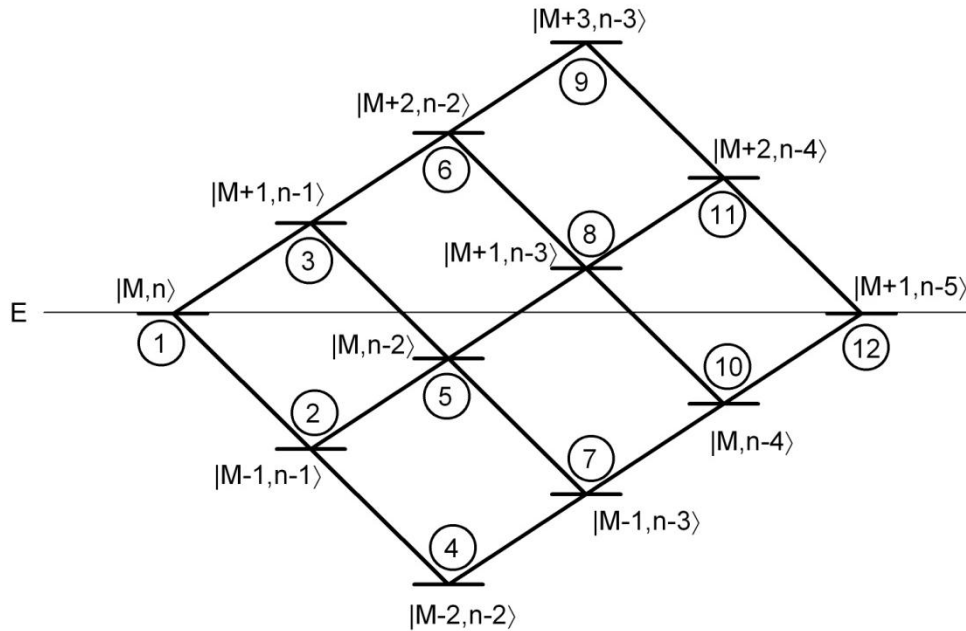
$$\hat{H} = \Delta E \frac{\hat{S}_z}{\hbar} + \hbar \omega_0 \hat{a} \hat{a}^\dagger + V \frac{2S_x}{\hbar} (\hat{a} + \hat{a}^\dagger) - i \frac{\hbar}{2} \Gamma(E)$$



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



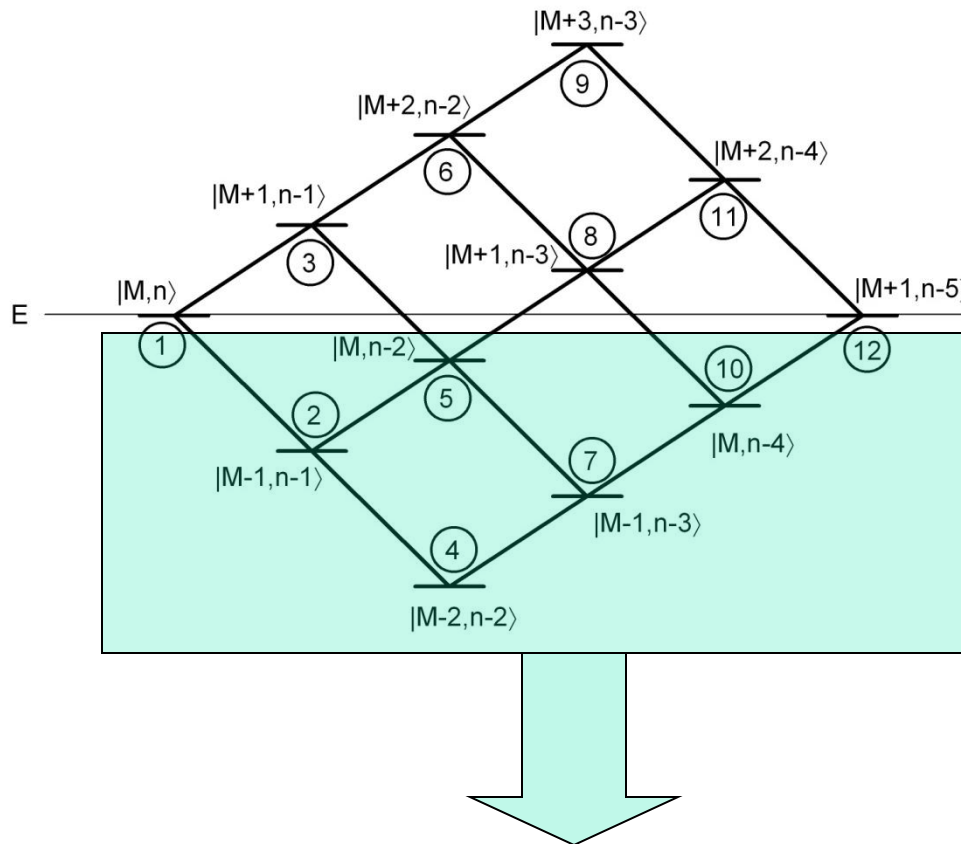
# Perturbation theory



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

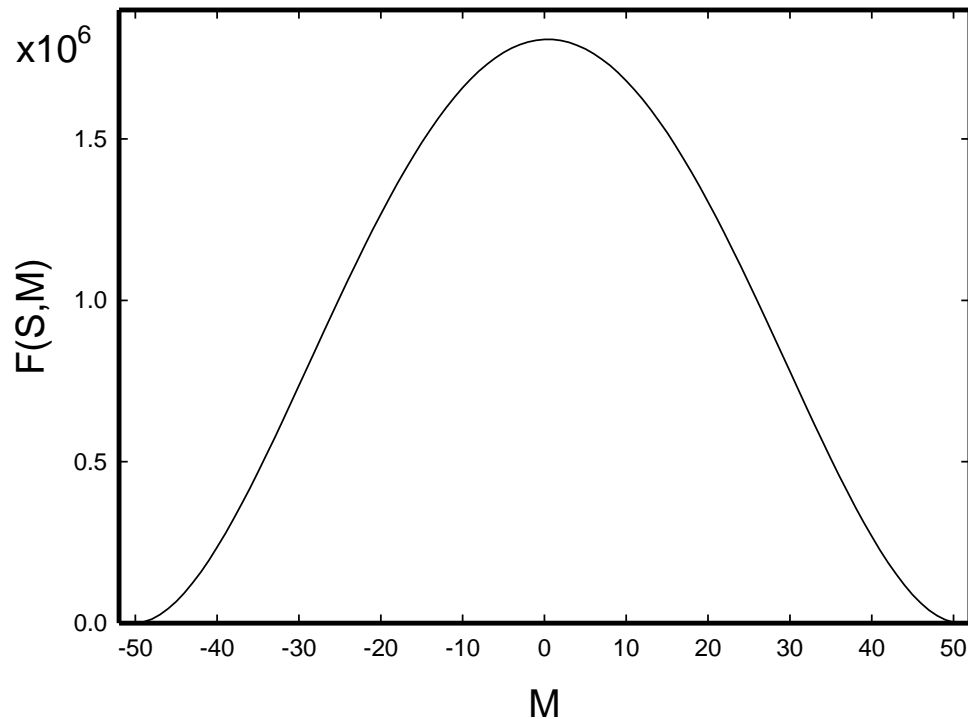
Finite basis approximation for  $|n\rangle \otimes |M\rangle \rightarrow |n-5\rangle \otimes |M+1\rangle$

# Perturbation theory



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

# Enhancement due to loss



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

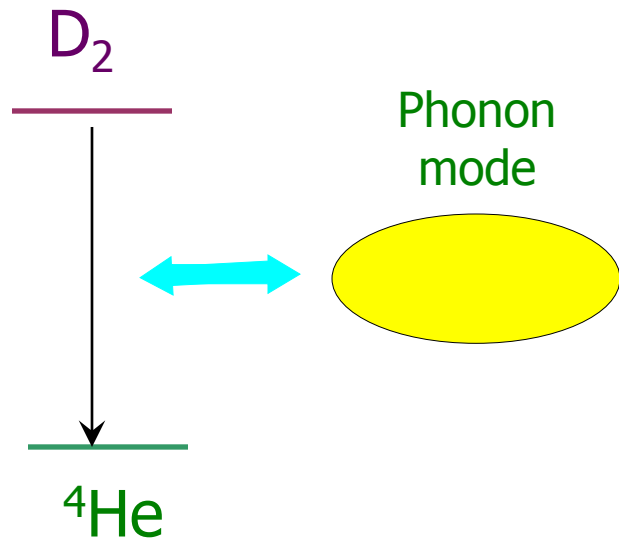


# Lossy version of model

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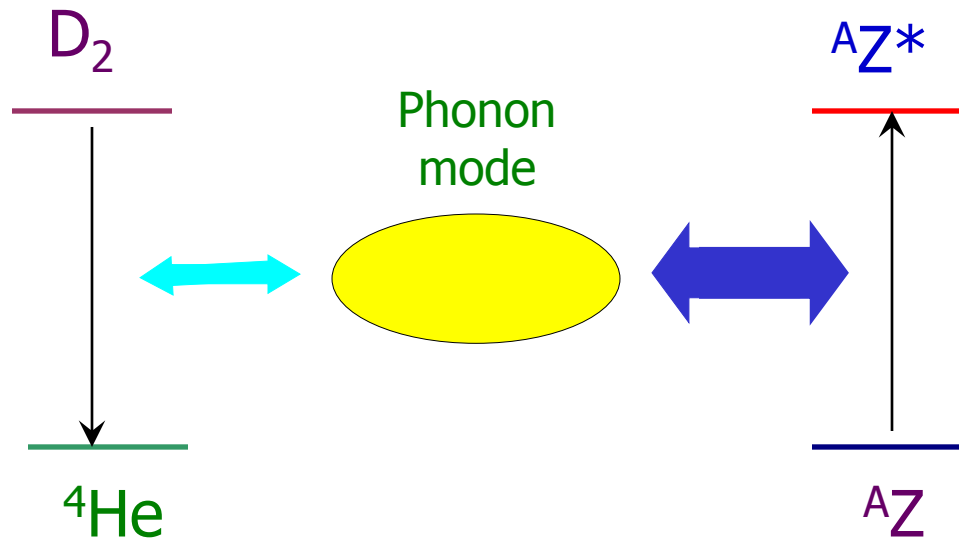
- Loss spoils the destructive interference
- Coherent energy exchange rates increased by orders of magnitude
- Much stronger effect
- Model capable of converting 24 MeV to atomic scale quanta

# Thinking about PdD



Unfortunately, coupling is too weak because of Coulomb repulsion

# Excitation transfer



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



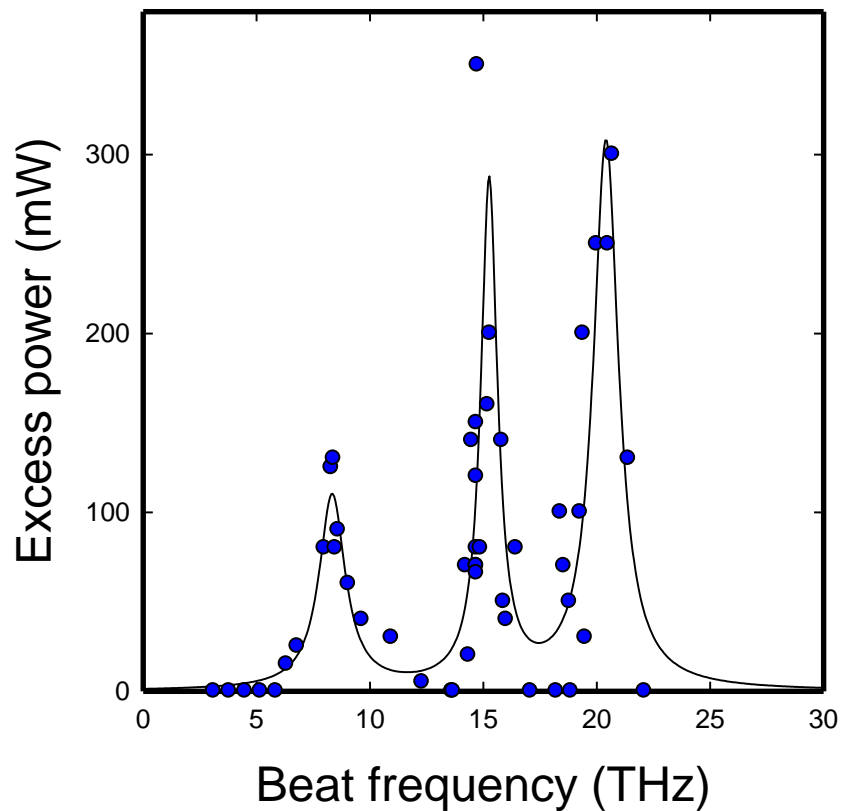
# Basic model

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

This kind of model is first one relevant to experiment

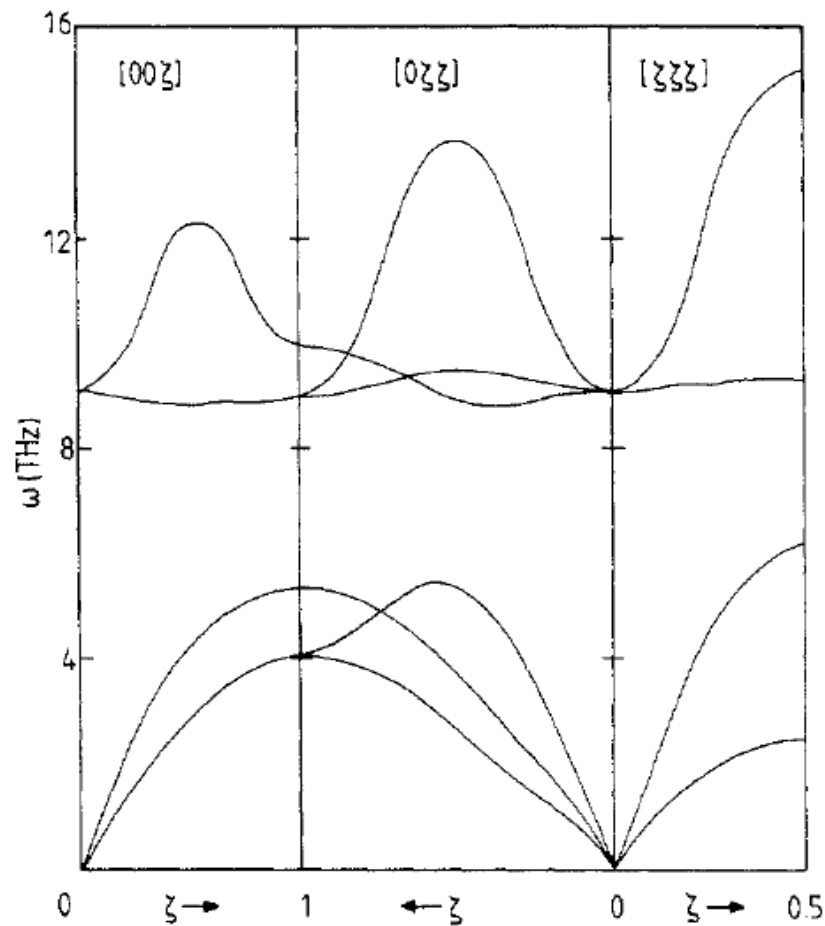
# What oscillator modes?



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



# Dispersion curve for PdD



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



# Strong-coupling limit

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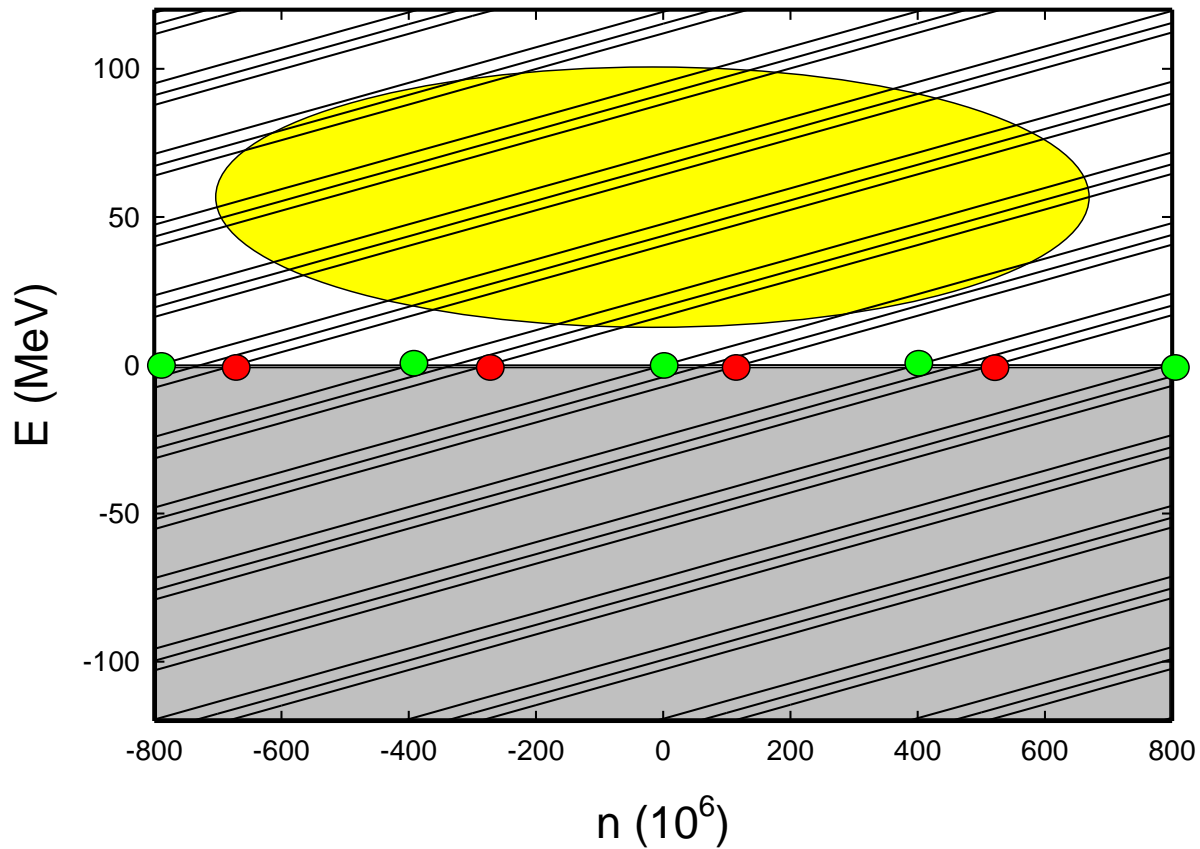
When the coupling between the receiver-side two-level systems and oscillator is strong, then the problem simplifies

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

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

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- 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

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

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

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



# Example: fast He diffusion

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## Active region:

$$A = 1 \text{ cm}^2$$

$$\Delta r = 100 \text{ nm}$$

## D<sub>2</sub> parameters:

$$f[\text{vacancy}] = 0.25$$

$$f[\text{D}_2] = 0.005$$

$$N[\text{D}_2] = 1.8 \times 10^{15}$$

$$\tau_{\text{D}_2} = 2 \times 10^{-8} \text{ sec}$$

## <sup>4</sup>He parameters:

$$D_{\text{He}} = 1.3 \times 10^{-14} \text{ cm}^2/\text{sec}$$

$$\tau_{\text{He}} = \Delta r^2/D_{\text{He}} = 2.1 \text{ hr}$$

## Phonon mode:

$$f_0 = 8.3 \text{ THz}$$

$$Q = 20$$

## Deuterium flux:

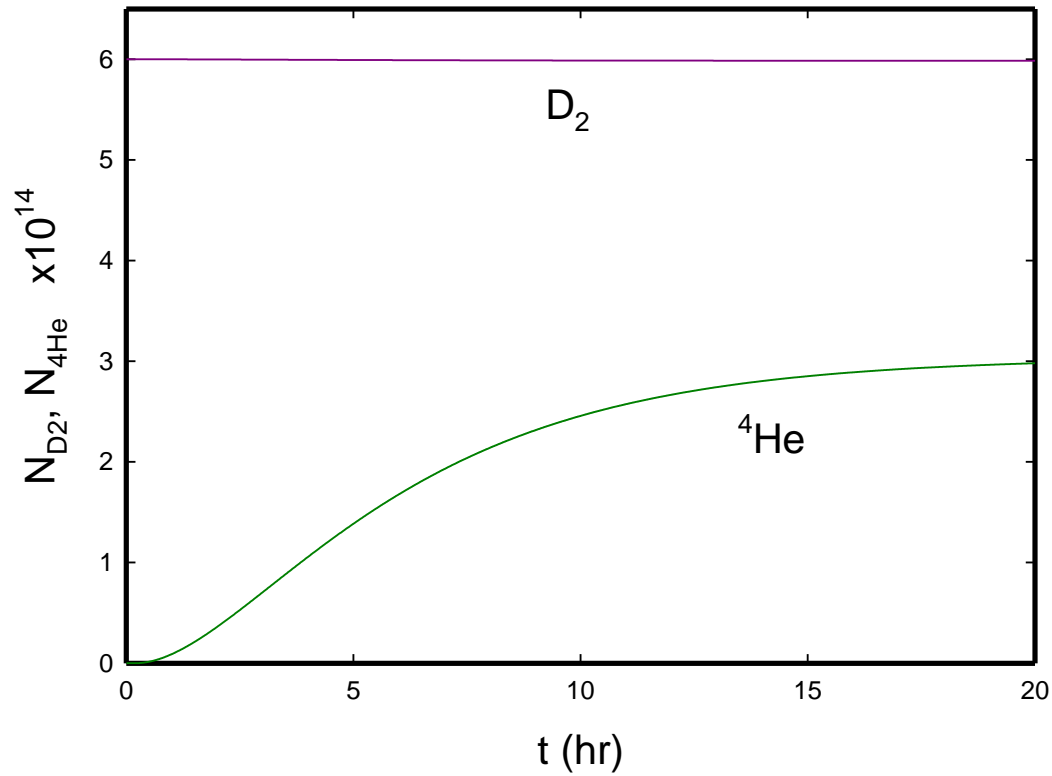
$$P_{\text{flux}} = 1 \text{ Watt/cm}^3$$

$$n_{\text{thresh}} = 100$$

## Basic reaction rate:

$$\Gamma_0 = 1/(3 \text{ hr})$$

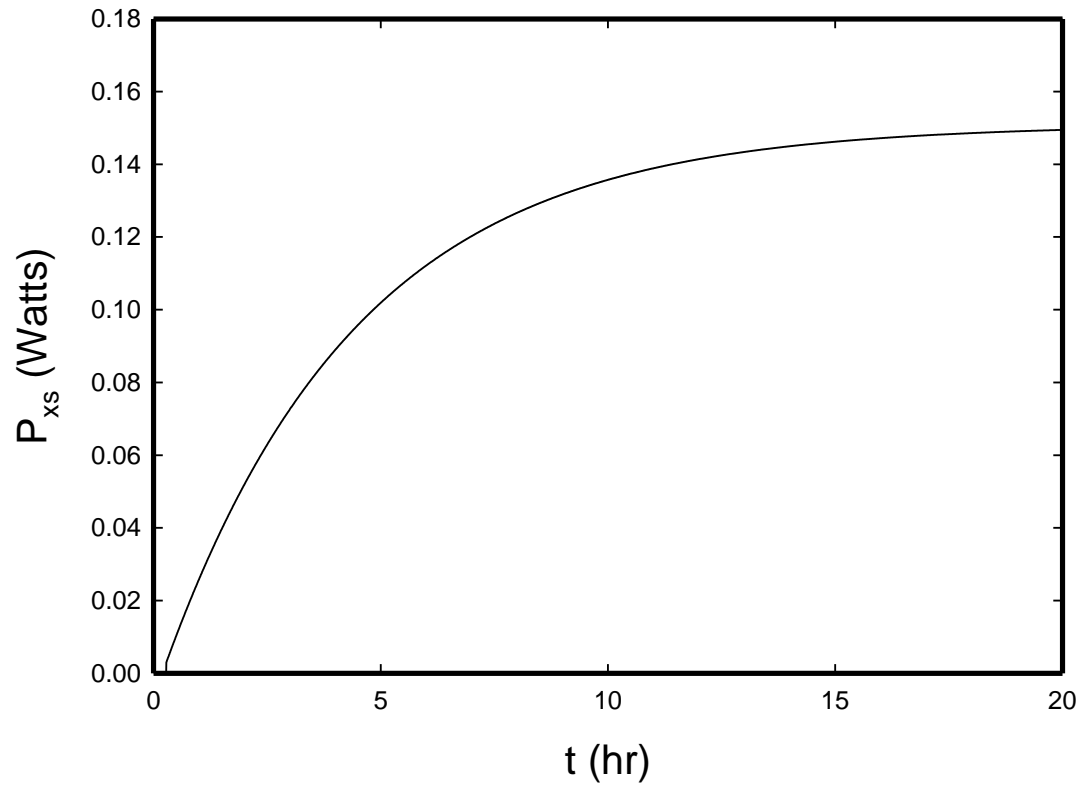
# Evolution of dideuterium, ${}^4\text{He}$





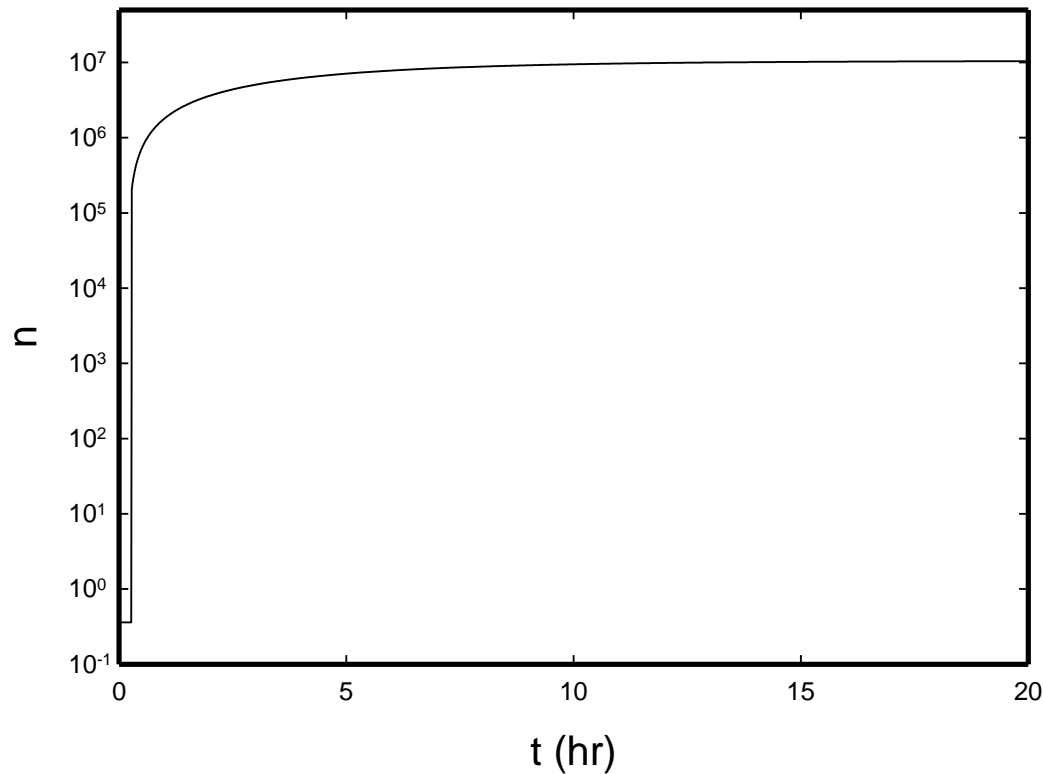
# Excess power

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# Number of phonons



Thermal: 0.36    Flux generated (1 W/cm<sup>3</sup>): 700    P<sub>xs</sub> generated: 10<sup>7</sup>



# Addressing the full problem

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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

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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

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Terms that couple from one channel to another:

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

We focus on strong force terms, although others present

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

Strong force      Lattice change



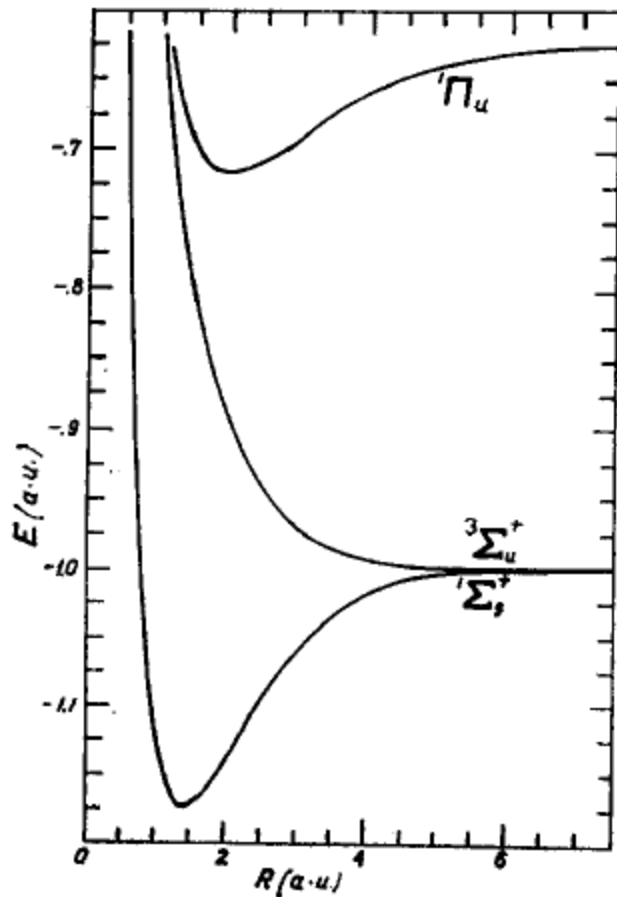
# Where is the $D_2$ ?

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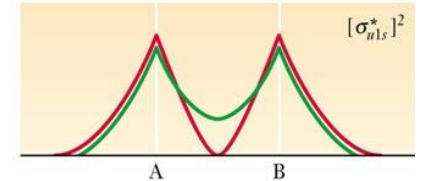
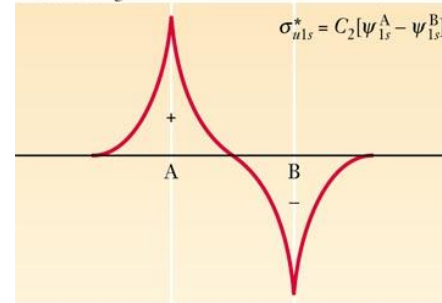
Molecular  $D_2$  does not form in bulk PdD

- 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

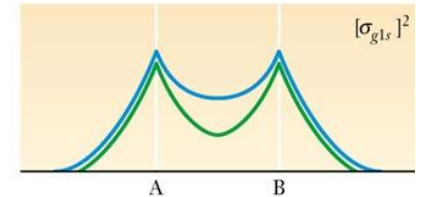
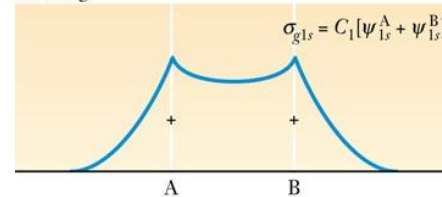
# Bonding and anti-bonding in H<sub>2</sub>



Antibonding

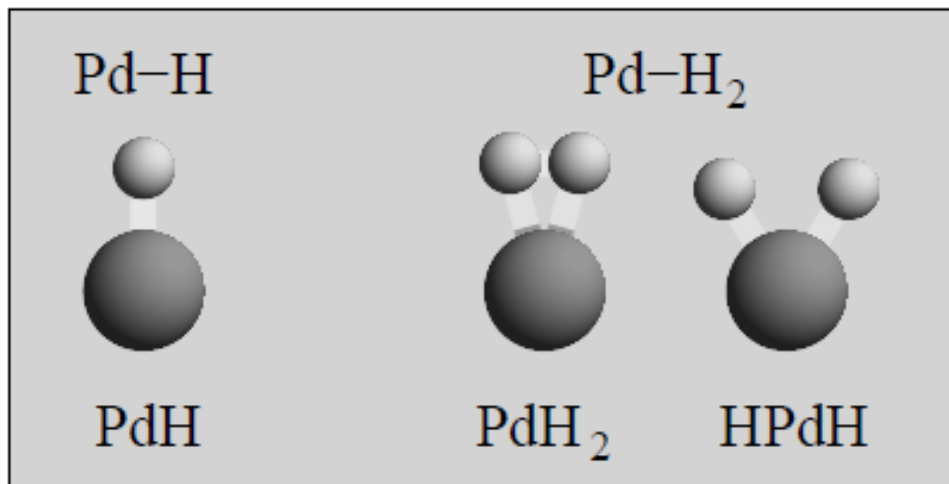


Bonding



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

# Pd-H<sub>2</sub> with $\sigma$ -bonding



In Pd-H<sub>2</sub>

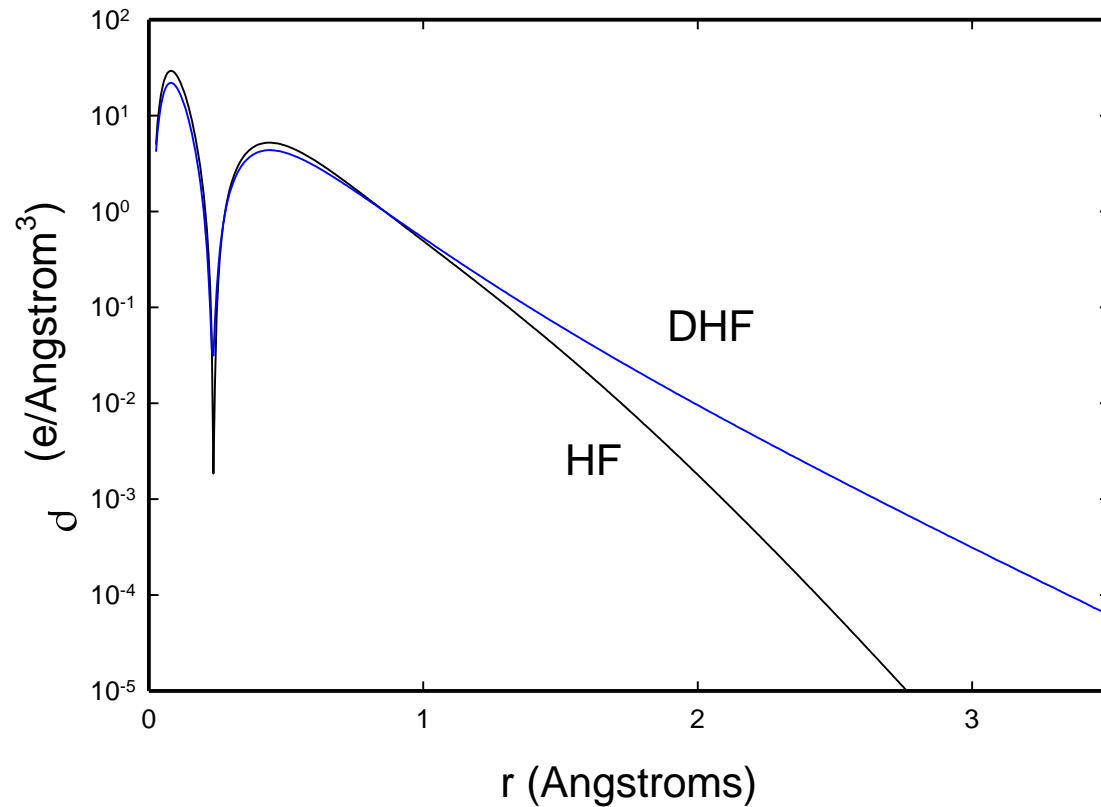
$d[\text{Pd-H}] = 1.67 \text{ \AA}$

$d[\text{H-H}] = 0.81 \text{ \AA}$

$\sigma$ -bonded Pd-H<sub>2</sub> is the ground state of the three-atom system.

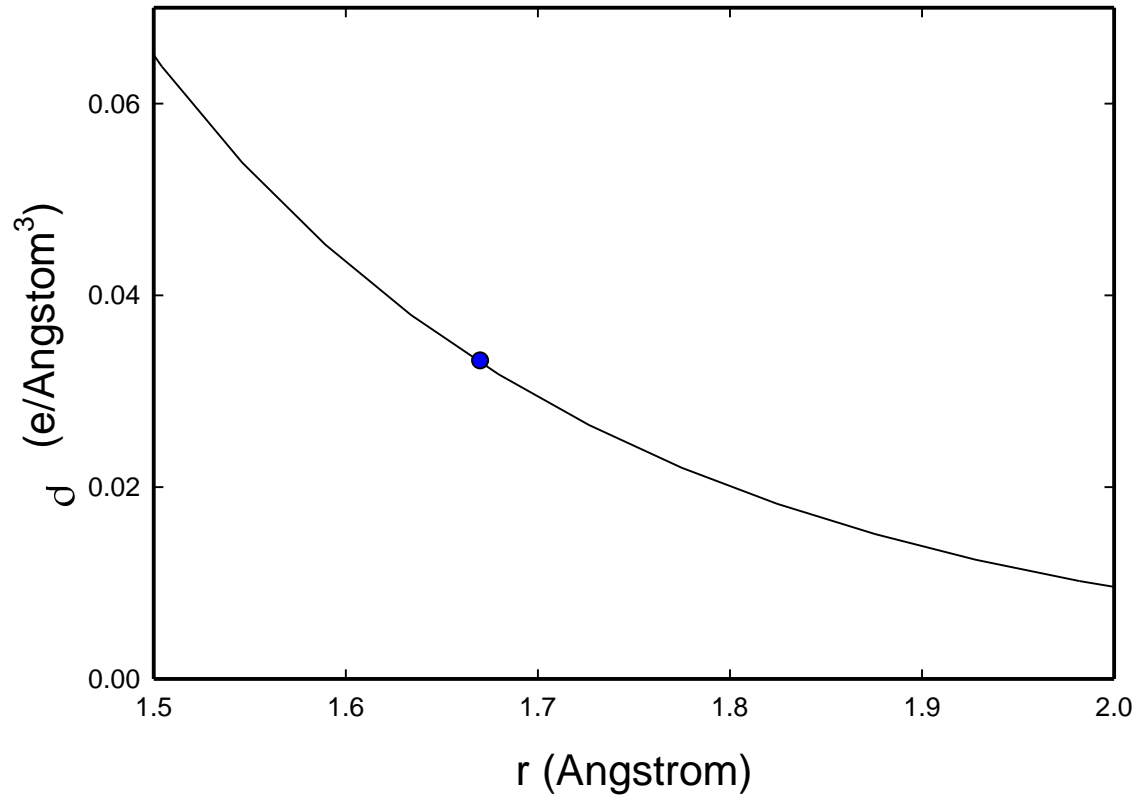
It is a combination of  $(4d)^{10} \text{ } ^1S_0$  Pd and  $(1\sigma)^2 \text{ } ^1S_0$  H<sub>2</sub>

# Electron density of Pd (4d)<sup>10</sup>



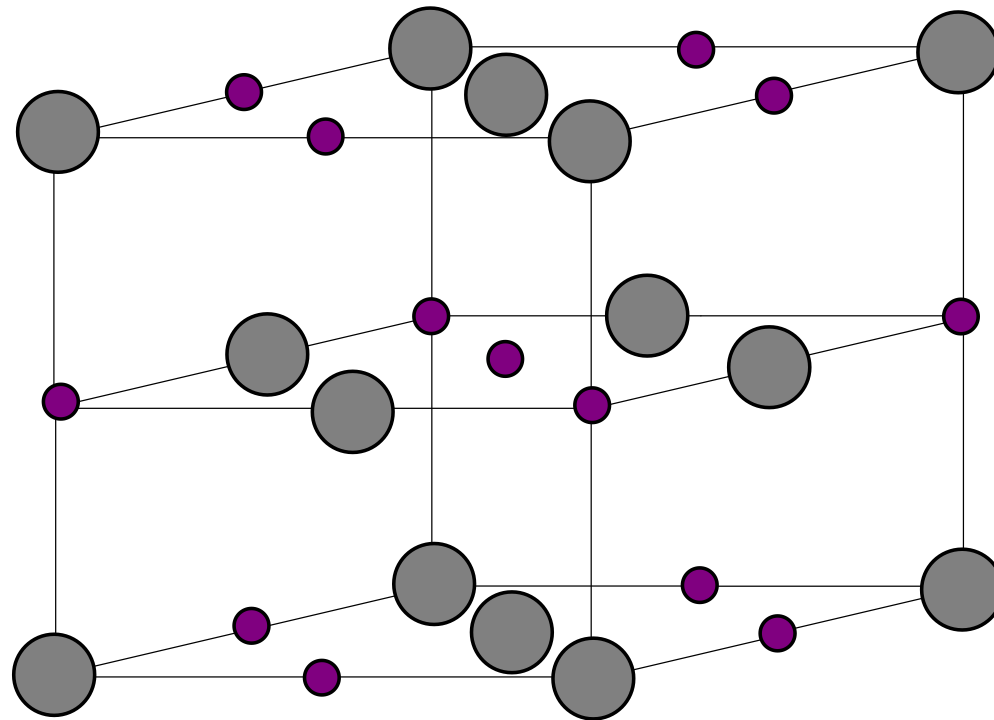


# Electron density at Pd-H distance

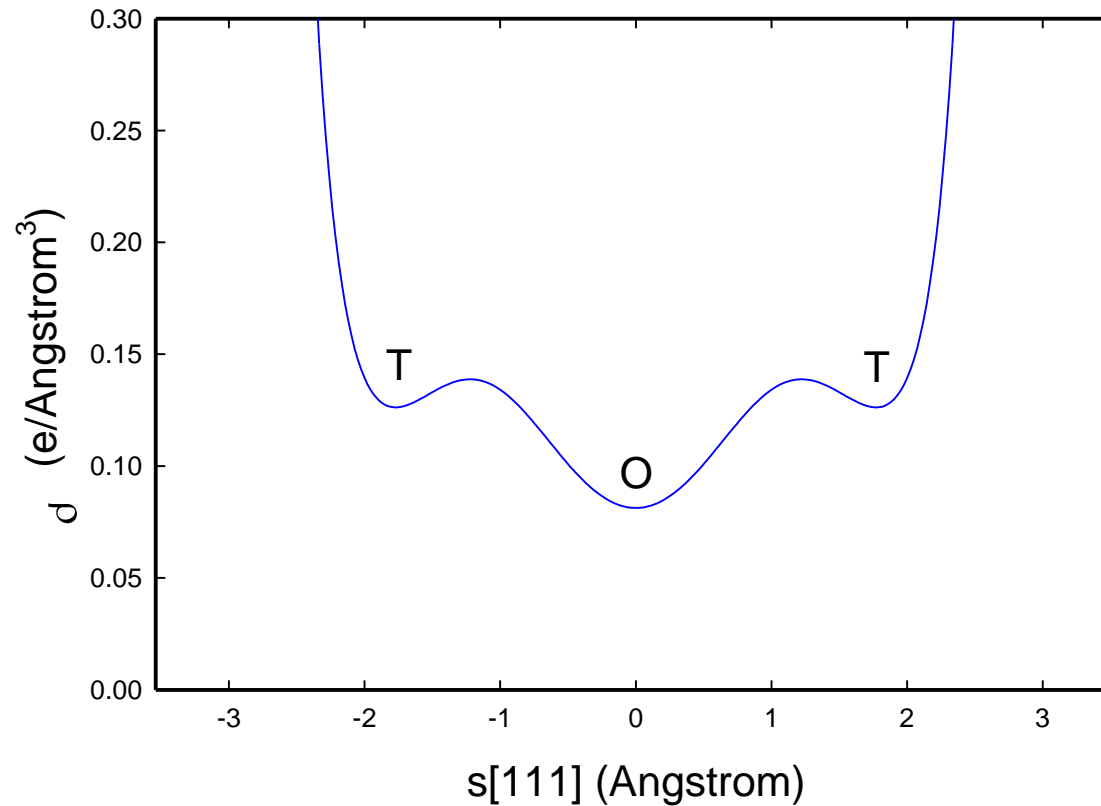


Pd-H distance in Pd-H<sub>2</sub> is 1.67 Angstroms, and electron density is 0.033

# PdD lattice structure (fcc)



# Electron density due to Pd around octahedral site





# Cannot form $D_2$ at O-site

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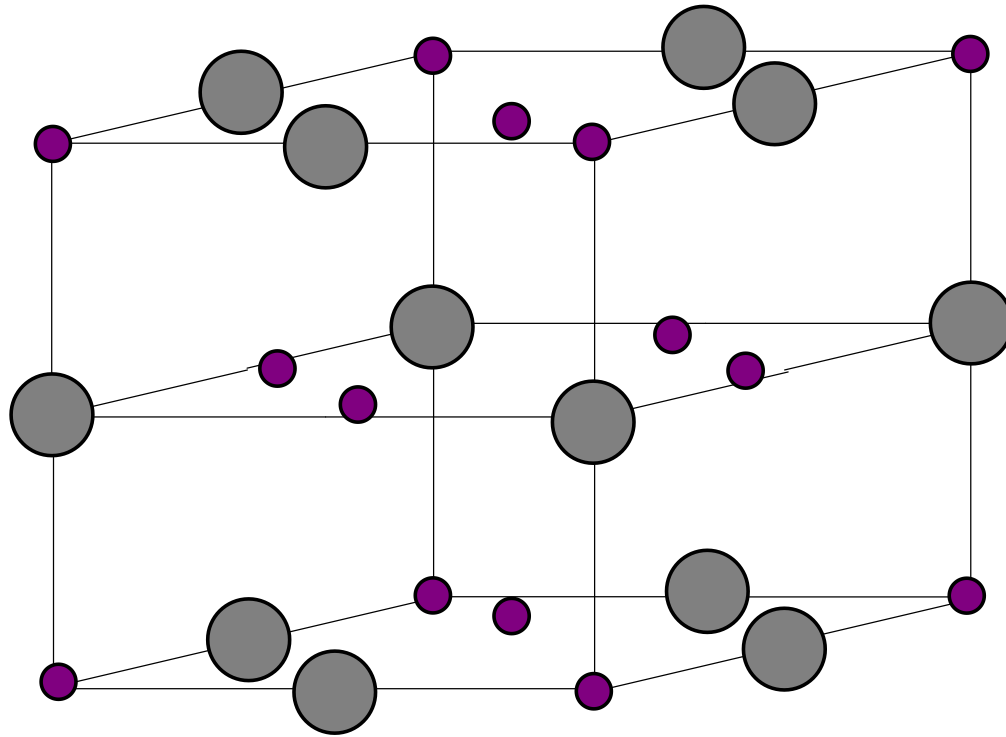
$H_2$  binds with Pd at 1.67 Angstroms Pd-H separation

Electron density at 1.67 Angstroms is  $0.33 \text{ e}/\text{Angstrom}^3$

Electron density at O-site in PdD is  $0.081 \text{ e}/\text{Angstrom}^3$

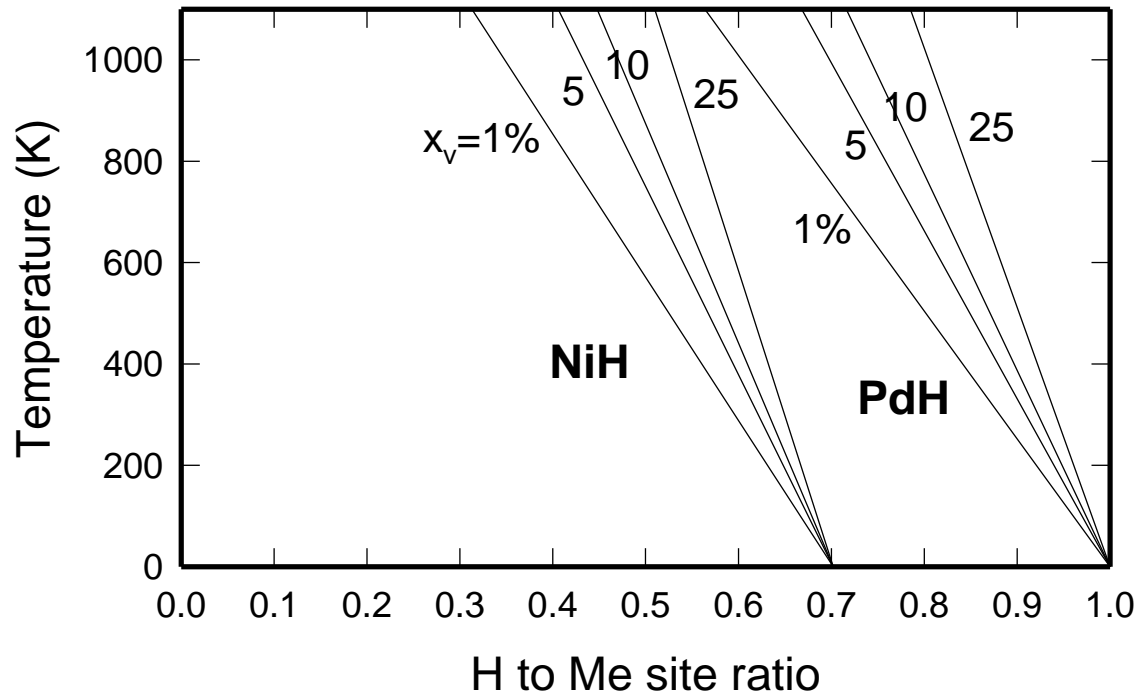
Anti-bonding orbitals occupied

# PdD Host lattice vacancy



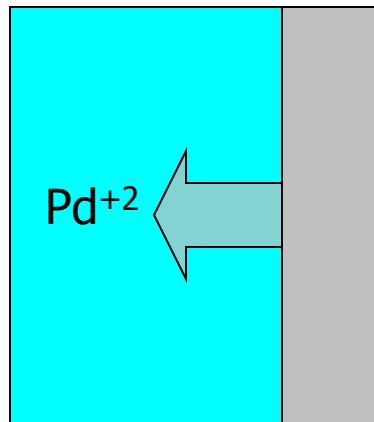
Deuterium atoms relax toward host vacancy

# Vacancies in host lattice

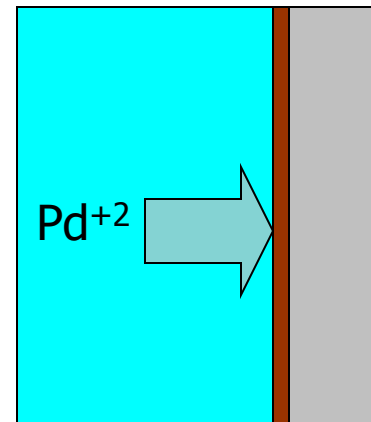


Vacancies in host metal lattice are thermodynamically favored at high loading

# Codeposition



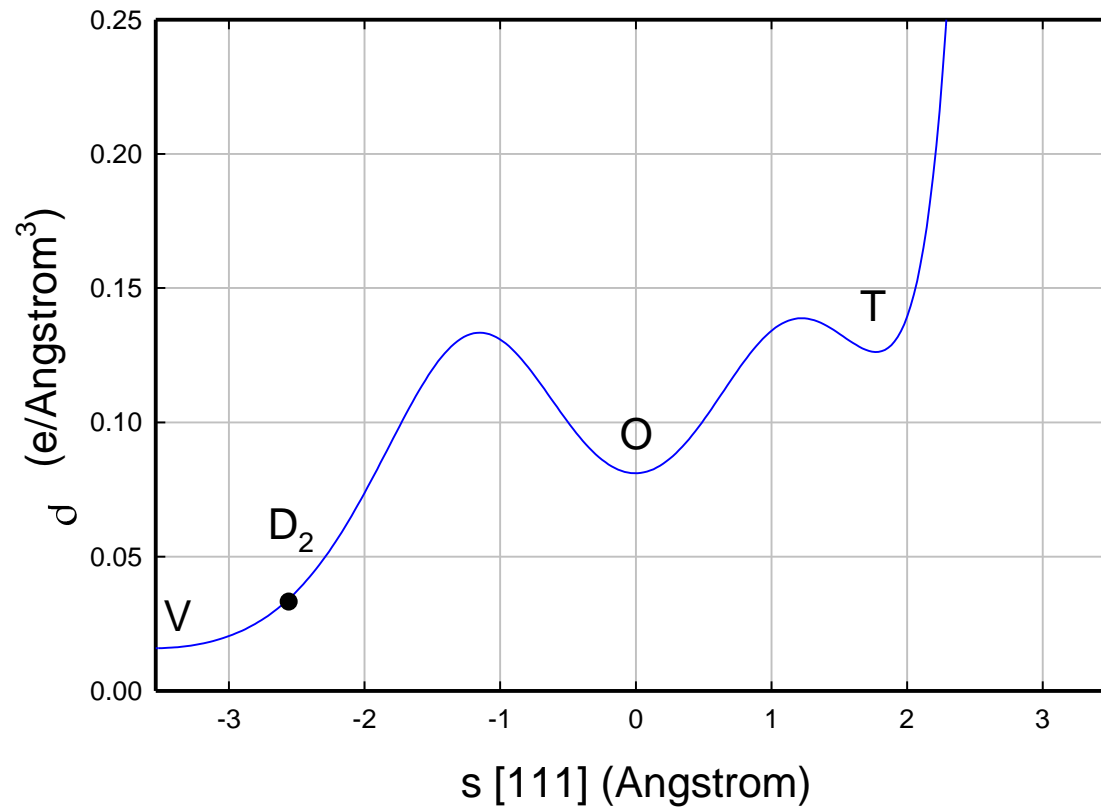
Anodic current



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  $\text{Pd}(\text{OH})_4^{-2}$ , Mountain and Wood (1988)]

# Electron density with vacancy







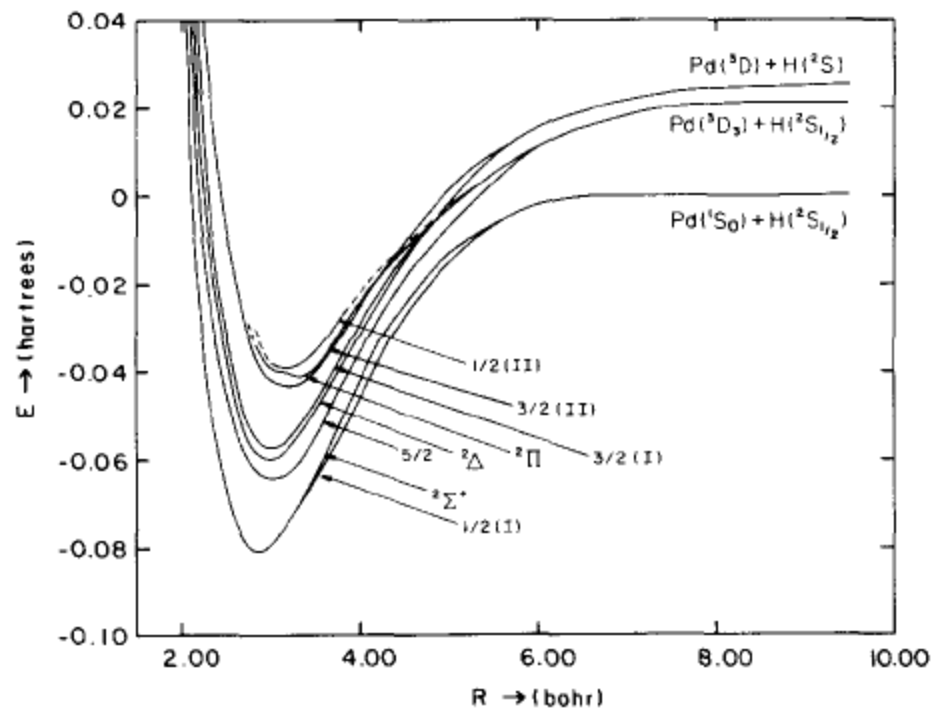
# Electron density seems low enough

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Superposition of atomic electron densities leads to a model electron density of  $0.016 \text{ e}/\text{Angstrom}^3$

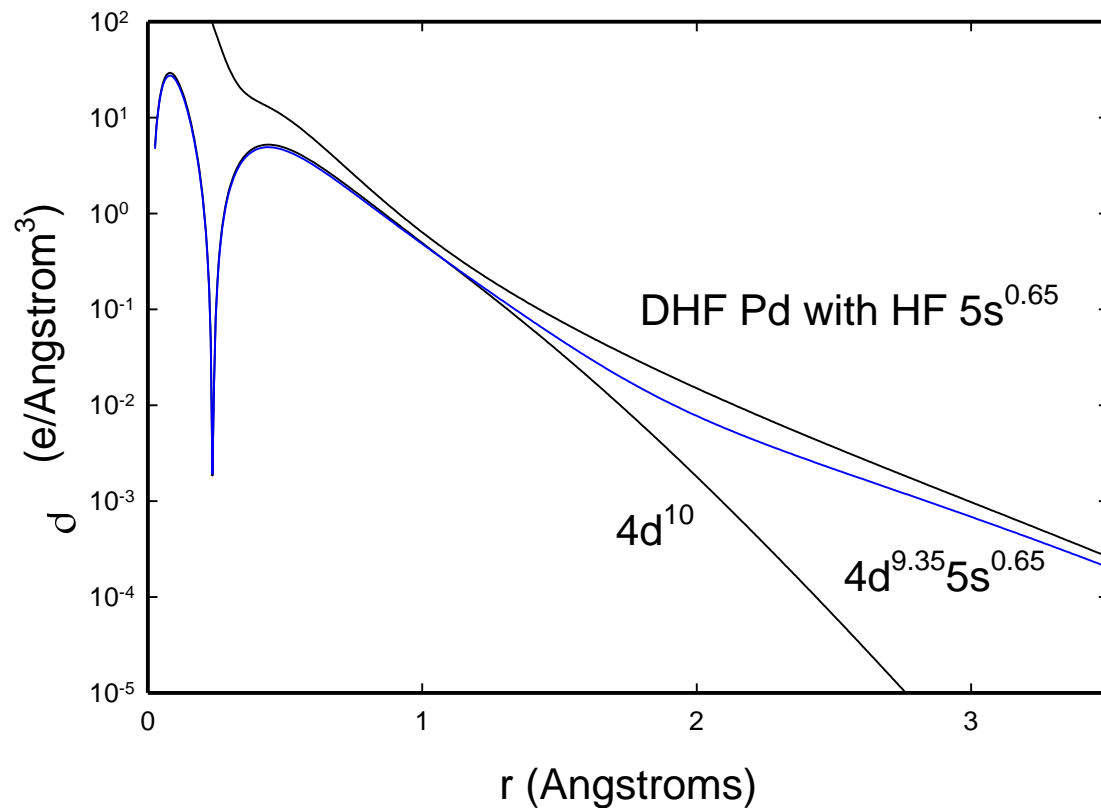
- Model electron density is 2x lower than for Pd-H<sub>2</sub>
- Would expect D<sub>2</sub> formation near vacancy
- Would expect relevant literature

# Check with PdH



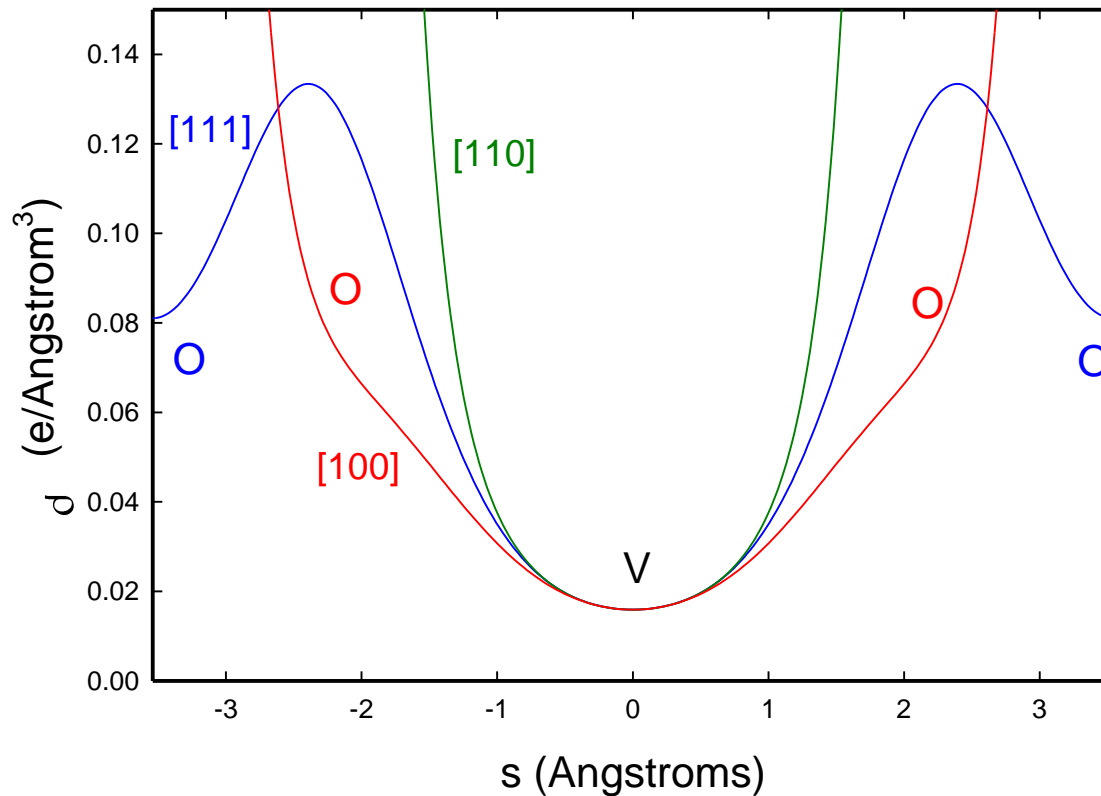
For ground state  
 $d[\text{Pd-H}] = 1.53 \text{ \AA}$

# Look at Pd density at 1.53 A



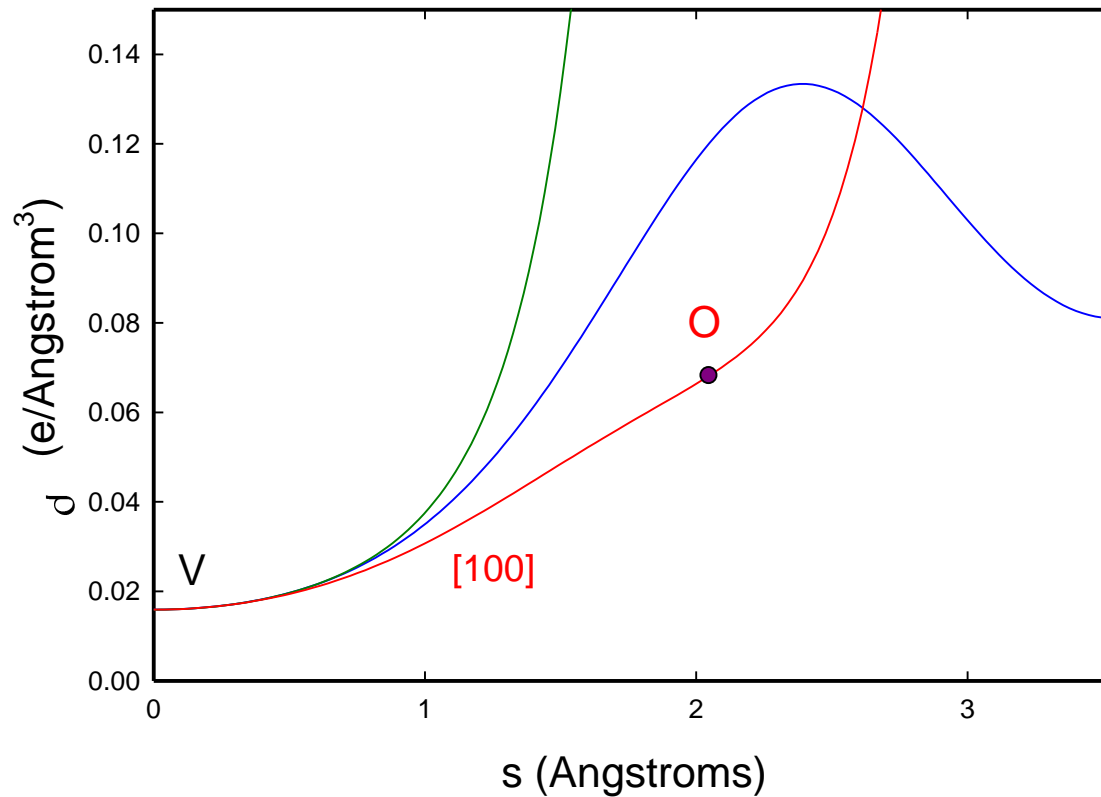
Model electron density at 1.53 A is  $0.0686 \text{ e}/\text{Angstrom}^3$

# Electron density around vacancy

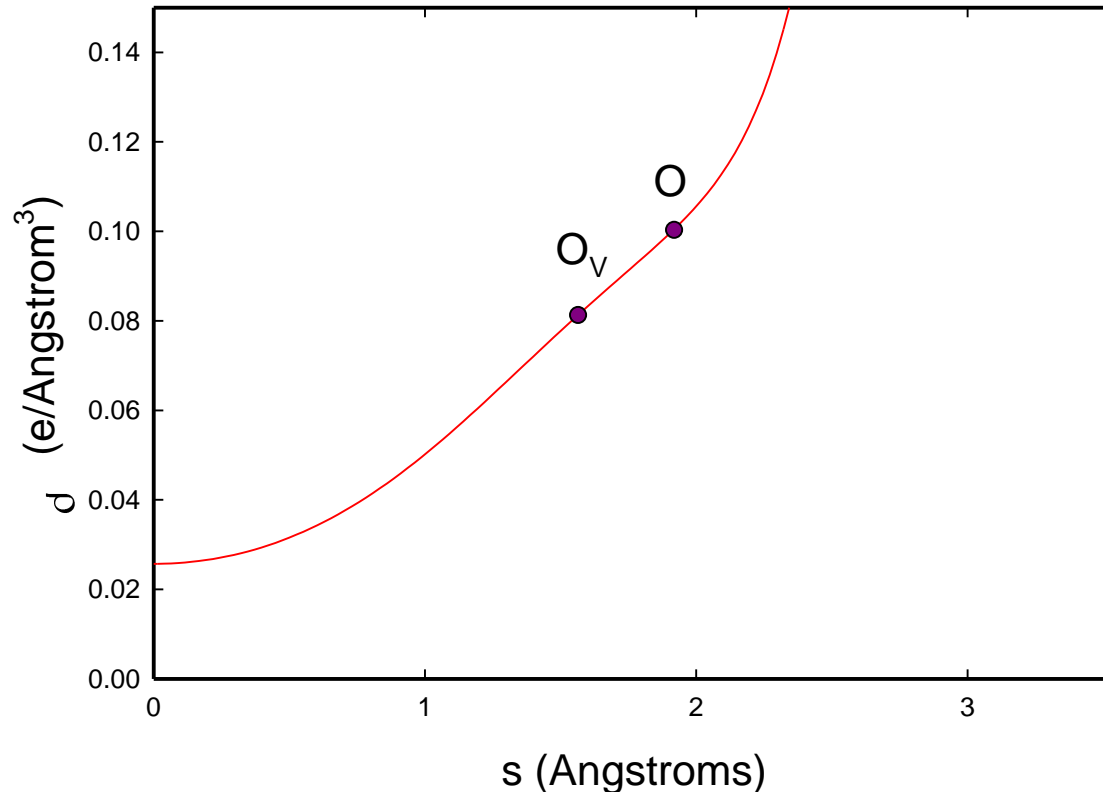


Nearest O-point no longer a minimum in electron density

# Model electron density just right now for H



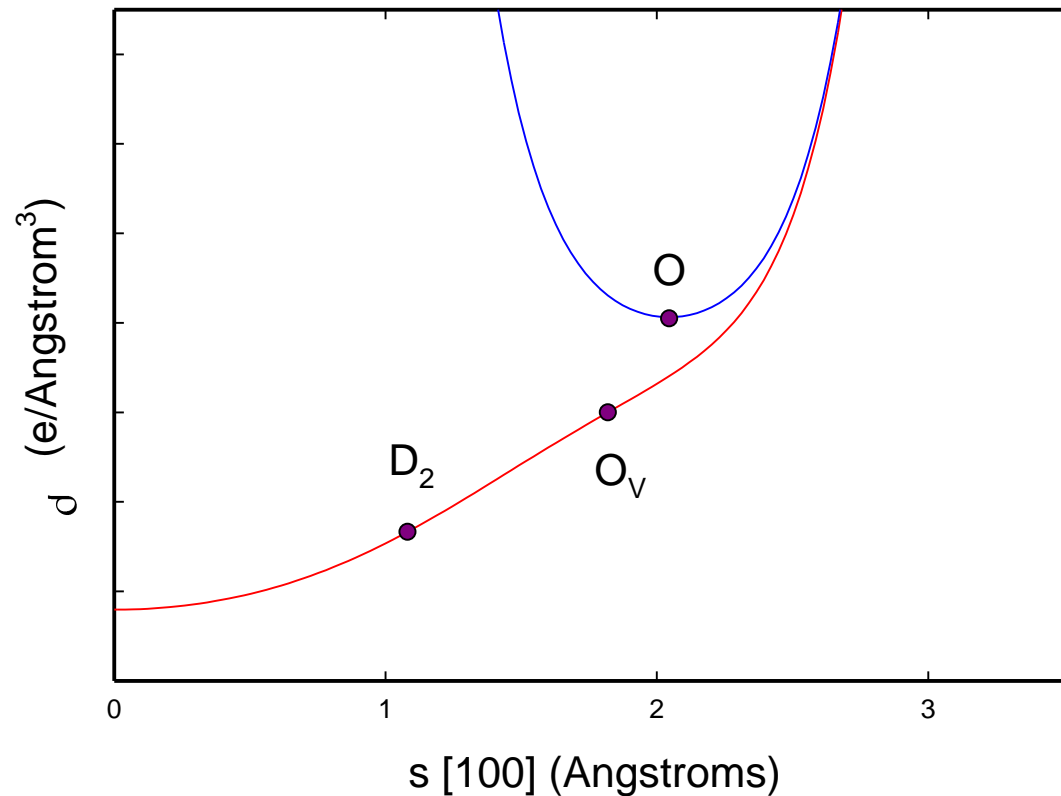
# Compare with Velikova et al (2009) DFT for Pd



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

Velikova shift corresponds to 0.081 e/Angstrom<sup>3</sup> , close to PdH 0.069 e/Angstrom<sup>3</sup>

# Summary (need VASP calculation!)



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



# Summary and conclusions

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- 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

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- We can construct coupled-channel equations systematically to implement lossy spin-boson type scheme in real physical system
- Detailed modeling now under way