

MSE 423 Fall 2025 – Week 2

# THINK OUTSIDE THE BOX



@Bobby Douglas, from photo.net

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## Last week: Wave mechanics

1. Particles, fields, interactions
2. Electromagnetic waves and energy scales
3. Particle-wave duality and de Broglie's relation
4. Wavefunction as a descriptor of an electron
5. Schrödinger equation (time dependent)
6. Plane wave solves it for the free electron, provided the dispersion relation  $E = \hbar\omega = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$  is satisfied

# Time-dependent Schrödinger's equation

(Newton's 2<sup>nd</sup> law for quantum objects)

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},t)\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$



1925-onwards: E. Schrödinger (wave equation), W. Heisenberg (matrix formulation), P.A.M. Dirac (relativistic)

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## Stationary Schrödinger's Equation (I)

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},*)\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Stationary Schrödinger's Equation (II)

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi(\vec{r}) = E \varphi(\vec{r})$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

From one equation to two simpler ones

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, *) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}$$

Separation  of variables

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi(\vec{r}) = E \varphi(\vec{r})$$

$$i\hbar \frac{d}{dt} f(t) = E f(t)$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Stationary Schrödinger's Equation (III)

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi(\vec{r}) = E \varphi(\vec{r})$$

1. It's not proven – it's postulated, and it is confirmed experimentally
2. It's an "eigenvalue" equation: it has a solution only for certain values (discrete, or continuum intervals) of E
3. For those eigenvalues, the solution ("eigenstate", or "eigenfunction") is the complete descriptor of the electron in its equilibrium ground state, in a potential V(r).
4. As with all differential equations, boundary conditions must be specified
5. Square modulus of the wavefunction = probability of finding an electron

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## Time dependence

$$i\hbar \frac{d}{dt} f(t) = E f(t) \quad \rightarrow$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

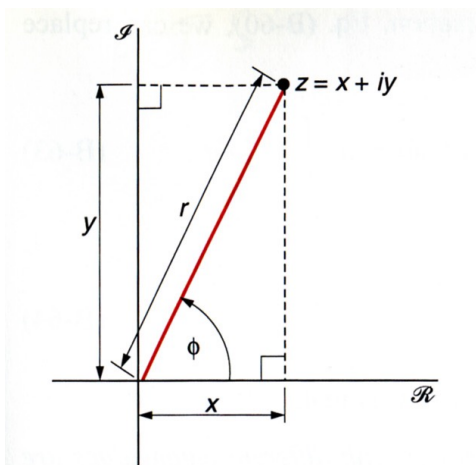
## Free particle: $\Psi(x,t)=\varphi(x)f(t)$

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(x) = E\varphi(x) \quad \rightarrow$$

$$i\hbar\frac{d}{dt}f(t) = Ef(t) \quad \rightarrow$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## A simple differential equation



**Figure B.6. The Argand Plane.** A point in this diagram represents a complex number either in the form  $x + iy$  or  $re^{i\phi}$ .

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

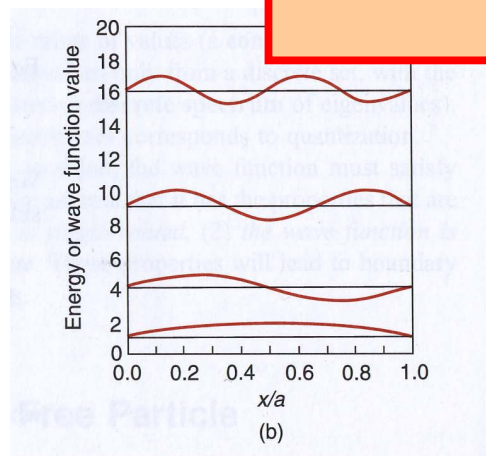
# Infinite Square Well (I) (particle in a 1-dim box)

$$-\frac{\hbar^2}{2m} \frac{d^2\varphi(x)}{dx^2} = E\varphi(x)$$

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Infinite Square Well (II)

$$\varphi(x) = C \sin\left(\frac{l\pi x}{a}\right)$$



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)



## Particle in a 2-dim box

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \varphi(x, y) = E \varphi(x, y)$$

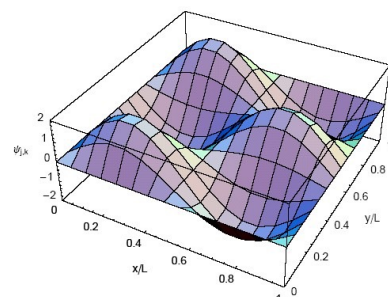
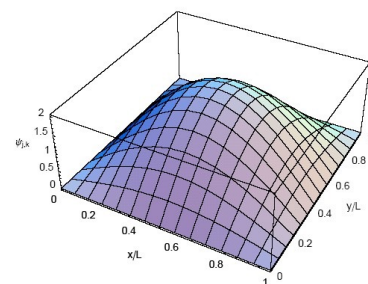
MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## Particle in a 2-dim box

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \varphi(x, y) = E \varphi(x, y)$$

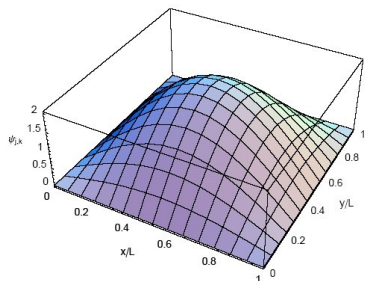
$$\varphi(x, y) = C \sin\left(\frac{l\pi x}{a}\right) \sin\left(\frac{m\pi y}{b}\right)$$

$$E = \frac{\hbar^2}{8m} \left( \frac{l^2}{a^2} + \frac{m^2}{b^2} \right)$$

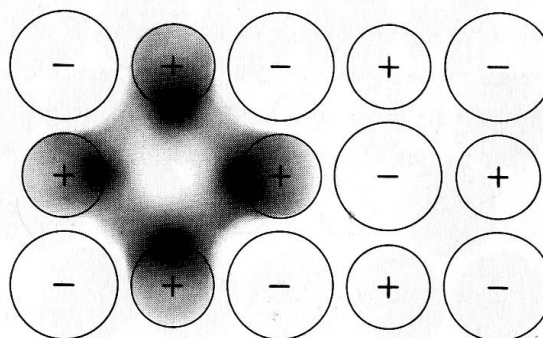
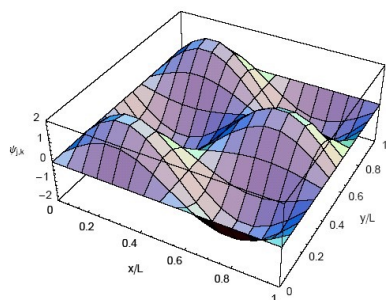


MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Particle in a 3-dim box: *Farbe* defect in halides ( $e^-$ bound to a negative ion vacancy)



$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi(x,y,z) = E \phi(x,y,z)$$



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## From Carl Zeiss to MIT

PHYSICAL REVIEW

VOLUME 120, NUMBER 6

DECEMBER 15, 1960

### Color Centers in Cesium Halide Single Crystals\*

P. AVAKIAN† and A. SMAKULA

Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received August 12, 1960)

Color centers have been investigated in the CsCl-type alkali halides. Cesium chloride, bromide, and iodide single crystals were grown from the melt and CsCl crystals also from solution. Coloration was produced by 130-kv x rays, 3.0-Mev electrons, and by electrolysis. In CsI coloration resulted from electrolysis only. The absorption of uncolored and colored crystals has been measured from 0.175 to 3.5  $\mu$  at 25°, -78°, and -190°C. After coloration all three crystals show one strong band in the visible (near infrared for CsI) and several weaker bands at shorter and longer wavelengths, which shift with temperature change. The spectral positions in  $m\mu$  for a number of the bands at -190°C are:

	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\lambda_4$	$\lambda_5$	$\lambda_6$	$\lambda_7$	$\lambda_8$	$\lambda_9$	$\lambda_{10}$
CsCl	227	270	370	430	579	715	780	855	980	
CsBr	241	~270	~315	390	480	646 (780)	840	(~930)	1055	
CsI	270	330		425	535	750		1050	1185	

The strongest band ( $\lambda_6$ ) behaves similarly to the *F* band in the NaCl-type alkali halides. The half-width of the band (0.20 to 0.23 ev at -190°C) and its increase with temperature, the shifting of the band maximum toward longer wavelengths upon warming to room temperature (by ~0.08 ev), and the conversion by bleaching with light into other bands support the assignment of this band as the *F* band. The spectral position of the band maximum approximately follows the Mollwo relation ( $\lambda_{\max} = \text{const } d^n$ , where  $d$  = interionic distance and  $n = 2.5$ ).

Bleaching experiments suggest the assignment of the band  $\lambda_{10}$  as the *M* band and the bands between the *F* and *M* bands as *R* bands. The origin of the ultraviolet bands is still uncertain.

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

### Molecular Limits to the Quantum Confinement Model in Diamond Clusters

T. M. Willey,<sup>1</sup> C. Bostedt,<sup>2,3,\*</sup> T. van Buuren,<sup>1</sup> J. E. Dahl,<sup>4</sup> S. G. Liu,<sup>4</sup> R. M. K. Carlson,<sup>4</sup> L. J. Terminello,<sup>1</sup> and T. Möller<sup>2,3</sup>

<sup>1</sup>Lawrence Livermore National Laboratory, Livermore, California 94550, USA

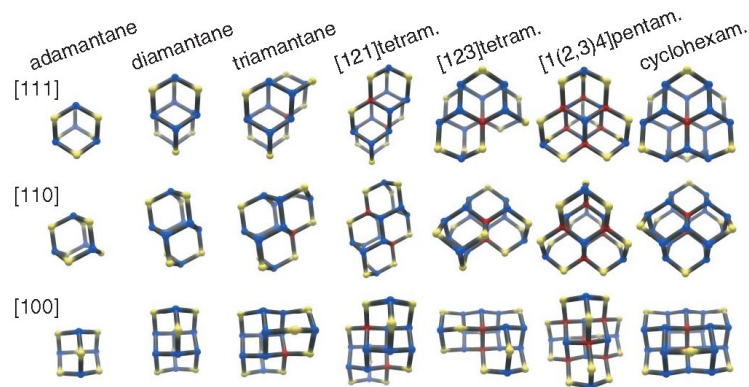
<sup>2</sup>Hamburger Synchrotronstrahlungslabor Hasylab at DESY, Hamburg, Germany

<sup>3</sup>Technische Universität Berlin, PN 3-1, Hardenbergstrasse 36, 10623 Berlin, Germany

<sup>4</sup>MolecularDiamond Technologies, Chevron, P.O. Box 1627, Richmond, California 94802, USA

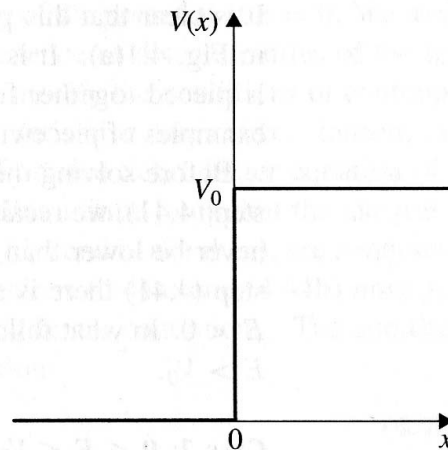
(Received 13 May 2005; published 7 September 2005)

The electronic structure of monodispersed, hydrogen-passivated diamond clusters (diamondoids) in the gas phase has been studied with x-ray absorption spectroscopy. The data show that the bulk-related unoccupied states do not exhibit any quantum confinement. Additionally, density of states below the bulk absorption edge appears, consisting of features correlated to CH and CH<sub>2</sub> hydrogen surface termination, resulting in an effective redshift of the lowest unoccupied states. The results contradict the commonly used and very successful quantum confinement model for semiconductors, which predicts increasing band edge blueshifts with decreasing particle size. Our findings indicate that in the ultimate size limit for nanocrystals a more molecular description is necessary.

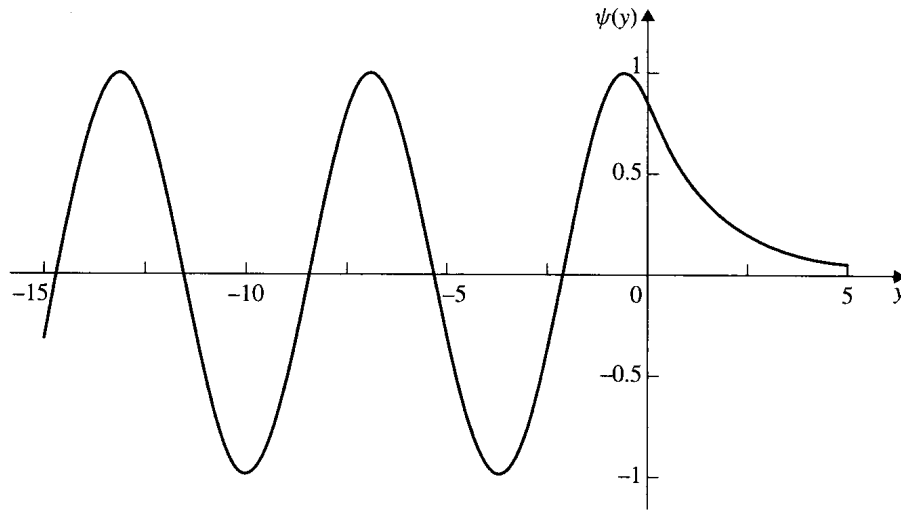


## Metal Surfaces (I)

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \varphi(x) = E\varphi(x)$$



# Metal Surfaces (II)



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Scanning Tunnelling Microscopy

(G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, Phys. Rev. Lett. 49, 57 (1982)).

Labels in the schematic: piezodrivre, feedback loop, sample, probe tip, constant-current contour.

Labels in the energy diagram: tip, sample,  $E_F$ ,  $E_F - eV$ ,  $\phi$ ,  $s$ .

$$\frac{I}{V} \propto \rho e^{-2\kappa s}$$

$$\kappa = \left(\frac{2m\phi}{\hbar^2}\right)^{1/2} = 1.1 \text{ \AA}^{-1}$$

$\rho$  = density of states

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)



MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

**OSSCAR**

Quantum Mechanics is one of the pillars of modern physics and chemistry. A large amount of the work carried out in computational physics and chemistry is concerned with the implementation of efficient algorithms to perform quantum mechanical calculations with the goal of simulating molecular and material systems.

Here, we present a collection of web applications which demonstrate fundamental concepts underlying quantum theory. Focus has been given to numerical methods employed in the solution of the time-independent and dependent Schrödinger equation for systems in the presence of simple potentials.

### 1. Numerical Solution of the Schrödinger Equation for a 1D Quantum Well

The notebook solves numerically the quantum-mechanical problem of a single rectangular one-dimensional quantum well, and displays interactively the eigenfunctions (plotted at the height of the corresponding eigenvalues).

**1. Numerical Solution of the Schrödinger Equation for a 1D Quantum Well**

**2. h**

**Dot**

**3. Avoided Crossing in One Dimensional Asymmetric Quantum Well**

We demonstrate the phenomenon of avoided crossing by solving the Schrödinger equation of a one-dimensional asymmetric quantum well.

**4. Shooting Method with Numerov Algorithm to Solve the Time Independent Schrödinger Equation for 1D Quantum Well**

The main goal of this notebook is to demonstrate the shooting method with the Numerov algorithm to search for the eigenfunctions and eigenvalues of a 1D quantum well.

**OSSCAR**

### Numerical Solution of the Schrödinger Equation for a One-Dimensional Quantum Well

Authors: Dou Du, Taylor James Baird and Giovanni Pizzi

[Go back to index](#)

Source code: <https://github.com/osscar-org/quantum-mechanics/blob/master/notebook/quantum-mechanics/quantumwell.ipynb>

This notebook solves numerically the quantum-mechanical problem of a single rectangular one-dimensional quantum well, and displays interactively the eigenfunctions (plotted at the height of the corresponding eigenvalues).

#### Goals

- Investigate quantum confinement by manipulating the depth and width of a finite one-dimensional quantum well.
- Learn how to solve the Schrödinger equation by matrix diagonalization.
- Understand quantum tunneling in regions where the energy is lower than the potential.

#### Background theory

[More on the background theory.](#)

#### Tasks and exercises

- Keep the depth at the default value (-0.2) and move the slider of the width from the smallest value (0.1) to the largest value (2.0). Do you see any change for the number of the states? How does the eigenvalue of the ground state (the lowest eigenstate) change with the increasing of the width of the quantum well and why?
  - Solution**
- Keep the width at the default value (1.2) and move the slider of the depth from the smallest value (-1.0) to the largest value (0.0). Do you see any change for the number of the states? How does the eigenvalue of the ground state (the lowest eigenstate) change with the increasing of the depth of the quantum well and why?
  - Solution**
- Investigate the role played by quantum confinement in this 1D potential well system by varying the width of the well via the "width" slider and observing the spacing of the energy levels of the system.
  - Solution**
- Keeping the sliders for the width and the height of the well at their default values and selecting the "Probability density" option, investigate the probability of a confined particle to be observed outside the potential well.
  - Solution**
- Please read the background theory section and try to understand the core of the numerical algorithm. Why is the diagonalization of the Hamiltonian matrix key to solve the Schrödinger equation?
  - Solution**

#### Interactive visualization

(be patient, it might take a few seconds to load)

Numerical Solution (ψ) Of The One Dimensional Schrödinger Equation

Width: 1.20 Depth: -0.20

Zoom f.: 5.00

Show:  wavefunction  Probability density  Show all (click on a state to select it)

- Width: the width of the quantum well.
- Depth: the depth of the quantum well.
- Zoom factor: the zoom factor for the magnitude of the eigenfunctions.

ation for a

r one-dimensional

responding eigenvalues).

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Energy from Wavefunctions

Schrödinger equation: operator, eigenvalues

E can be obtained as an “expectation value”

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## Dirac Notation

Dirac's  $\langle \text{bra} | \text{kets} \rangle$  (elements of vector space)

Scalar product (induces a metric  $\rightarrow$  Hilbert space)

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

# Physical Observables from Wavefunctions

Eigenvalue equation:

Expectation values for the operator (energy)

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)

## 4 concepts

- Operators
- Eigenvalues
- Eigenfunctions
- Expectation values

MSE 423 Fundamentals of Solid-state Materials - Nicola Marzari (EPFL, Fall 2025)