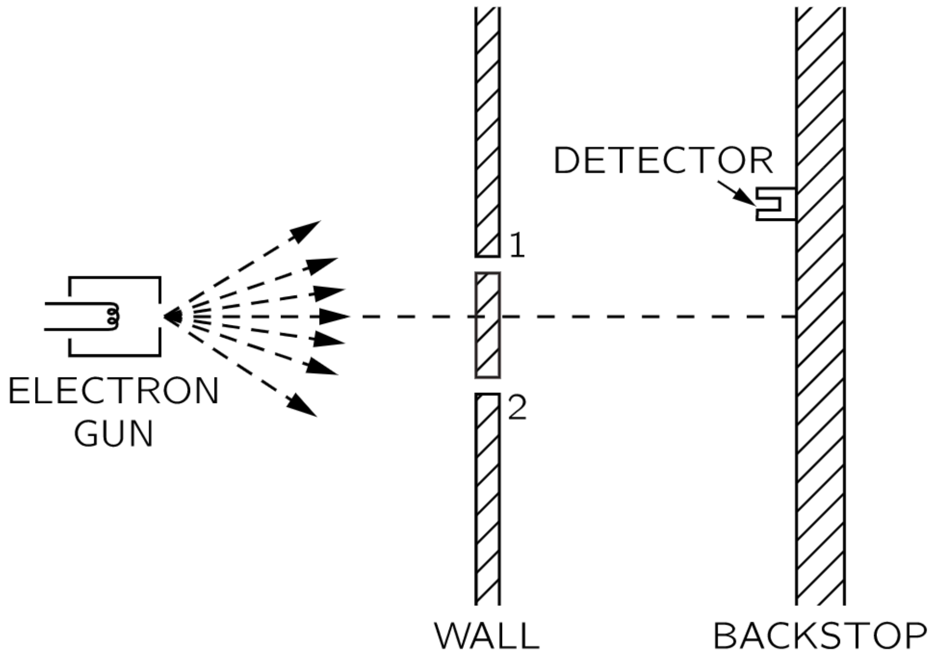
A review of basic principles

1/8/20

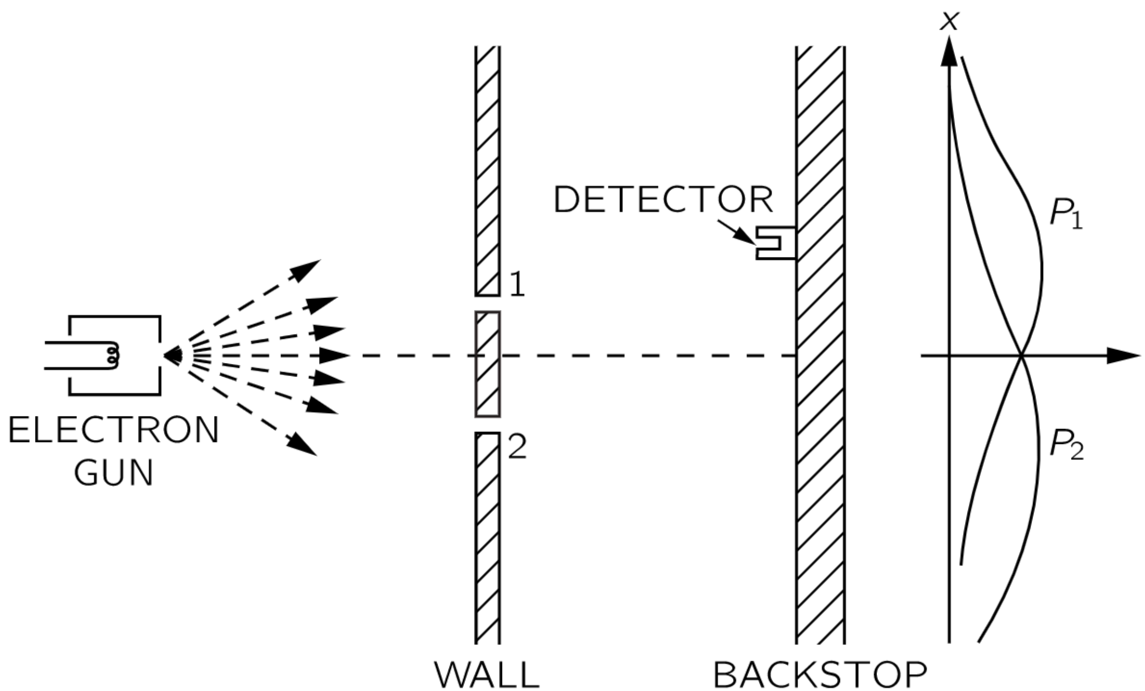
"…deep down, nobody truly understands quantum mechanics. We use its equations confident of getting the correct answers, feeling certain about the "whats" but ever puzzled about the "hows." The quantum mechanical world gets stranger and stranger the harder one looks, until finally there is scarcely any handhold in ordinary reality. Readers encountering these ideas for the first time should appreciate and accept how discomforting that world will now seem.

It's also the only world we have."

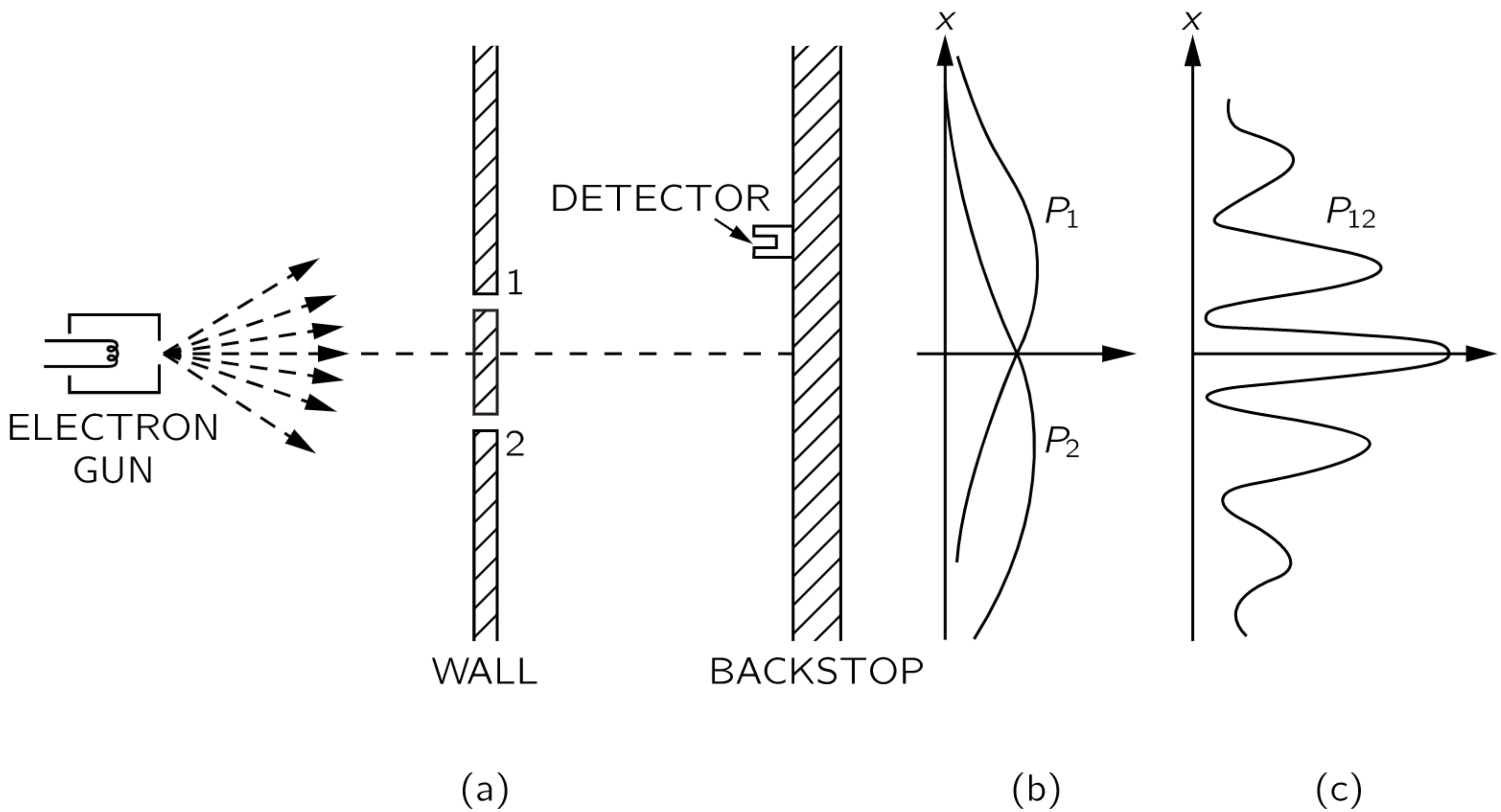
Principles of Chemistry, Munowitz



(a)

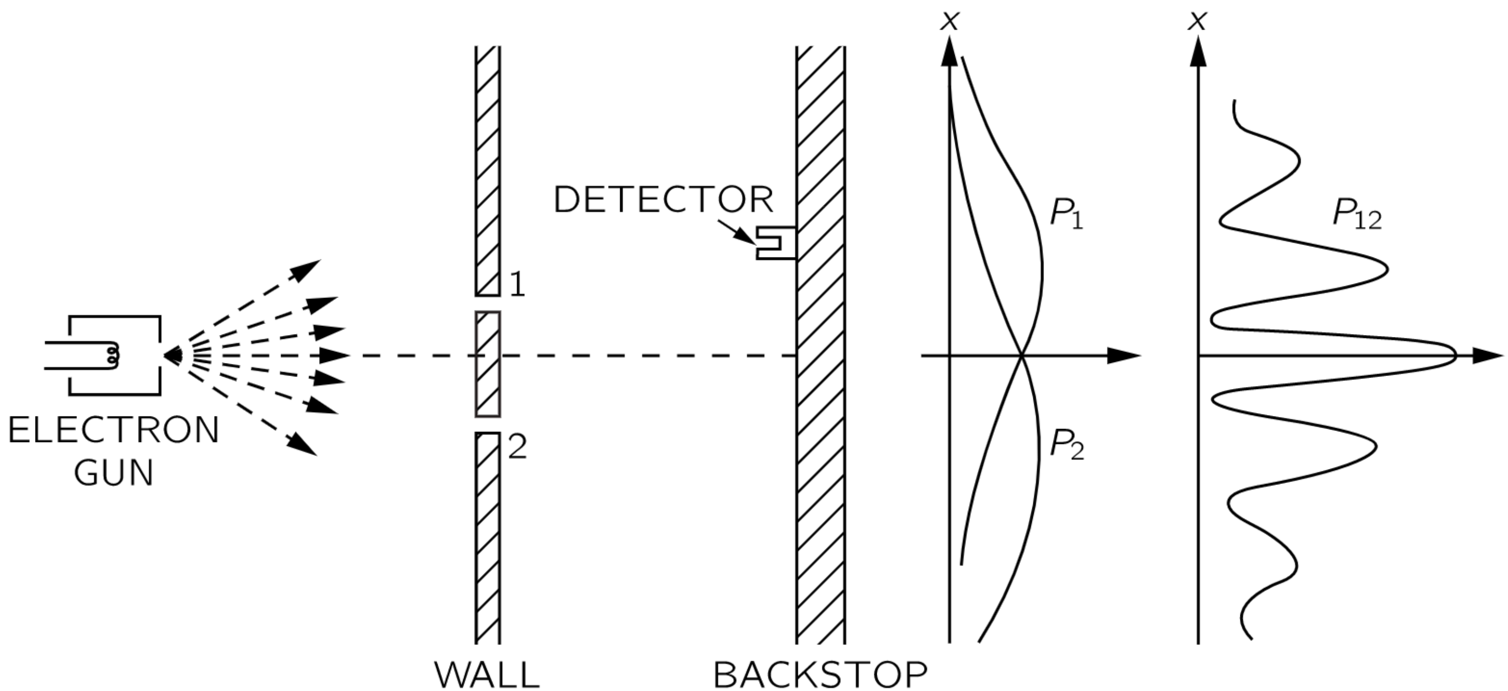


(a) (b)



$$P_1 = |\phi_1|^2$$

$$P_2 = |\phi_2|^2$$



(a) (b) (c)

$$P_1 = |\phi_1|^2 \qquad \phi = \phi_1 + \phi_2$$

$$P_2 = |\phi_2|^2 \qquad P_{12} = |\phi_1 + \phi_2|^2$$

General principles

- The probability of an event is given by the square of the absolute value of a complex number ϕ which is called the probability amplitude
- When an event can occur in several alternative ways, the probability amplitude for the event is the sum of the probability amplitudes for each way considered separately. There is interference.

$$\phi = \phi_1 + \phi_2$$

$$P_{12} = |\phi_1 + \phi_2|^2$$

- If an experiment is performed which is capable of determining whether one or another alternative is actually taken, the probability of the event is the sum of the probabilities for each alternative. The interference is lost.

$$P = P_1 + P_2$$

A fundamental postulate

- The state of the system is described by a wavefunction $\Psi(\mathbf{x}, t)$ that depends of the positions of the particles and time. $\Psi(\mathbf{x}, t)$ is also called the state function and turns out to contain all knowable information about the system.

Our primary goal is to find the correct wavefunction for our system of interest, and use it to obtain our desired observables

Other postulates

- Every physical observable has a corresponding linear operator in quantum mechanics. These operators can be obtained from classical counterparts in a Cartesian coordinate representation via replacements:

$$x \rightarrow \hat{x}$$

$$p \rightarrow -i\hbar \frac{\partial}{\partial x}$$

Other postulates

- The possible values that can result from the measurement of a physical observable are the eigenvalues of the corresponding operator

$$\hat{B}\chi_i = b_i\chi_i$$

Measurement of a property causes a sudden change of the state function, a "collapse" of the wavefunction

Other postulates

- The average value of a physical observable at time t is given by

$$\langle \hat{B} \rangle = \int \Psi^*(\mathbf{x}, t) \hat{B} \Psi(\mathbf{x}, t) d\mathbf{x}$$

where $\Psi(\mathbf{x}, t)$ is the normalized state function of the system

$|\Psi(\mathbf{x}, t)|^2$ acts like a probability density function

Other postulates

- The state function Ψ(x, t) of the system obeys the time-dependent Schrödinger wave equation (SWE):

$$\hat{H}\Psi(\mathbf{x},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t)$$

The time-independent SWE

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x})$$

Using the SWE to solve for Ψ

1. Determine V(**x**) for the system of interest

2. Use the SWE to find the wavefunction

Examples:

- Particle in a box
- Harmonic Oscillator
- Hydrogen atom

Hamiltonian for many-electron systems

Kinetic energy

A, B, i, j

Potential energy

Electron-electron (i-j)
Electron-nucleus (i-A, i-B, j-A, j-B)
Nucleus-nucleus (A-B)

Kinetic energy

A, B, i, j

Potential energy

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Nucleus-nucleus (A-B)

$$\hat{H} = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i}^{N}\sum_{A}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} + \sum_{A}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{|\mathbf{R_A} - \mathbf{R_B}|}$$

The Born-Oppenheimer approximation

$$\hat{H} = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A}^{M} \cancelto{0}{\frac{1}{2M_A}}\nabla_A^2 - \sum_{i}^{N}\sum_{A}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|} + \cancelto{\text{constant}}{\sum_{A}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{|\mathbf{R_A} - \mathbf{R_B}|}}$$

$$\hat{H}_e = -\sum_{i}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i}^{N}\sum_{A}^{M} \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|} + \sum_{i}^{N}\sum_{j>i}^{N} \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

$$\hat{H}_e \Phi_e = E_e \Phi_e$$

$$\hat{H}_{nucl} = -\sum_{A}^{M} \frac{1}{2M_A}\nabla_A^2 + \sum_{A}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{|\mathbf{R_A} - \mathbf{R_B}|} + E_e$$

$$\hat{H}_{nucl} \Phi_{nucl} = E_{nucl} \Phi_{nucl}$$

The electronic Hamiltonian

$$\hat{H}_e = \underbrace{-\sum_i^N \frac{1}{2}\nabla_i^2 - \sum_i^N \sum_A^M \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|}}_{\text{One-electron operator}} + \underbrace{\sum_i^N \sum_{j>i}^N \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}}_{\text{Two-electron operator}}$$

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{|\mathbf{r_i} - \mathbf{R_A}|}$$

$$\hat{g}(i,j) = \frac{1}{|\mathbf{r_i} - \mathbf{r_j}|}$$

$$\hat{H}_e = \sum_i^N \hat{h}(i) + \sum_{i<j}^N \hat{g}(i,j)$$

Course overview

- Learning tools of abstraction to make the math doable
  - State vectors
  - Second quantization
  - Diagrams

- Applying tools of abstraction to derive commonly used methods in electronic structure

Coming up…

- State vectors and Dirac notation
- Hartree-Fock