Ab initio electronic structure theory of extended systems: periodicity and electron repulsion

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Electronic structure theory

- Solving the electronic structure problem for molecules or solids consists in solving the electronic *Schrödinger equation*,

$$\hat{H}\Psi_I = E_I\Psi_I.$$

- The electronic wavefunction $\Psi_I \equiv \Psi_I(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ depends on the position (and spin) of the (N) electrons.
- $\hat{H}$ is the *Hamiltonian* operator.
- There is in principle an infinite number of solutions.
- The solution with the *lowest energy* (usually labelled as $I = 0$) is referred to as the *ground-state* solution.
- The higher-energy solutions $(I > 0)$ are the excited-state solutions.
- In this course, we will work within the *Born–Oppenheimer approximation*.

Electronic structure theory

- In other words, the positions of the nuclei will be *fixed* while we are solving the Schrödinger equation for the electrons.

- Vibronic effects will not be discussed.

- The N-electron Hamiltonian reads $\hat{H} = \hat{T} + \hat{W}_{\rm ee} + \hat{V}_{\rm ne}$ where

$$\hat{T} \equiv -\frac{\hbar^2}{2m_{\rm e}} \sum_{i=1}^{N} \nabla^2_{\mathbf{r}_i} = -\frac{\hbar^2}{2m_{\rm e}} \sum_{i=1}^{N} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \longrightarrow \quad \textit{kinetic energy}$$

$$\hat{W}_{\rm ee} \equiv \sum_{i<j}^{N} \frac{e^2}{4\pi\varepsilon_0 \left|\mathbf{r}_i - \mathbf{r}_j\right|} \times \qquad \longrightarrow \quad \textit{two-electron repulsion}$$

$$\hat{V}_{\rm ne} \equiv \sum_{i=1}^{N} v_{\rm ne}(\mathbf{r}_i) \times \qquad \longrightarrow \quad \textit{electron-nuclei attraction}$$

where $\quad v_{\rm ne}(\mathbf{r}) = -\sum_{A}^{\rm nuclei} \frac{Z_A e^2}{4\pi\varepsilon_0 \left|\mathbf{r} - \mathbf{R}_A\right|}$

- Note that the operators are written in *SI units*.

Atomic units

- It is convenient to use *unitless* coordinates and energies where the *Bohr radius*

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} \approx 0.529\text{Å}$$

and twice the *ionization* energy of the *hydrogen atom*

$$E_\mathrm{I} = \frac{m_e e^4}{2(4\pi\varepsilon_0)^2\hbar^2} \approx 13.6\,\mathrm{eV}$$

are used as *reference*:

$$\begin{array}{ccl} x & \rightarrow & \tilde{x} = x/a_0 \\ y & \rightarrow & \tilde{y} = y/a_0 \\ z & \rightarrow & \tilde{z} = z/a_0 \\ E & \rightarrow & \tilde{E} = E/(2E_I) \end{array}$$

- This is the system of so-called *atomic units* (a.u.).

Atomic units

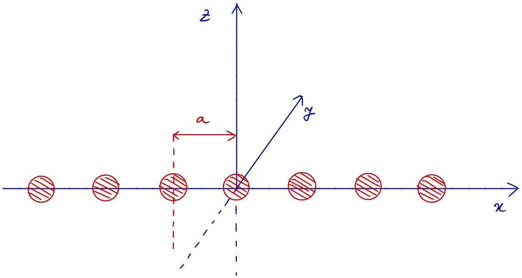
- In practice, the "tilde" symbol is dropped.
- It can be shown that, when atomic units are employed, the Hamiltonian looks like if $\text{“}\hbar = m_{\mathrm{e}} = e^2/(4\pi\varepsilon_0) = 1\text{”}$.
- As a result, the operators will be written as follows from now on:

$$\hat{T} \equiv -\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i} = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

$$\hat{W}_{\mathrm{ee}} \equiv \sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times$$

$$v(\mathbf{r}) = -\sum_{A}^{\text{nuclei}}\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}.$$

1D extended system: linear chain of hydrogen atoms

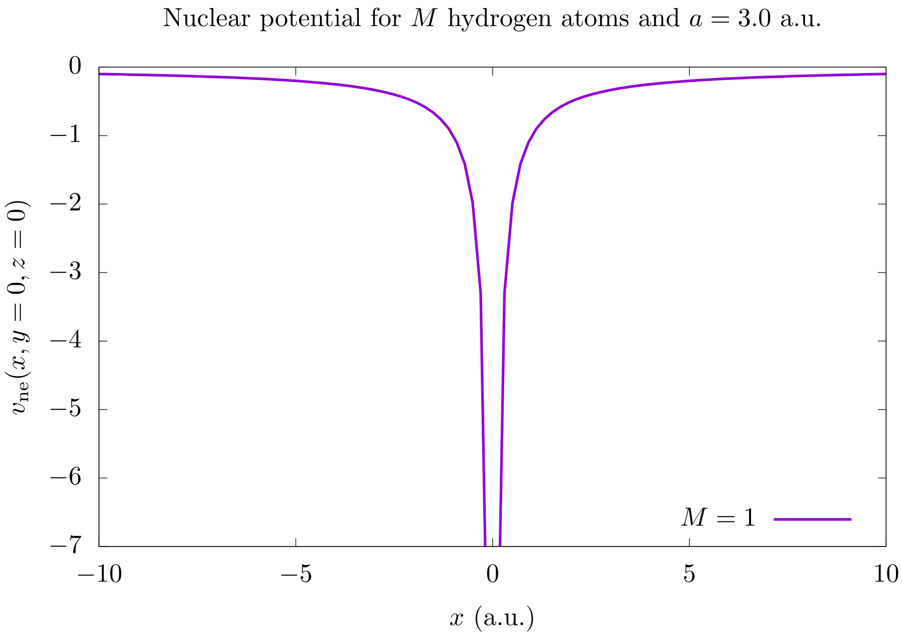


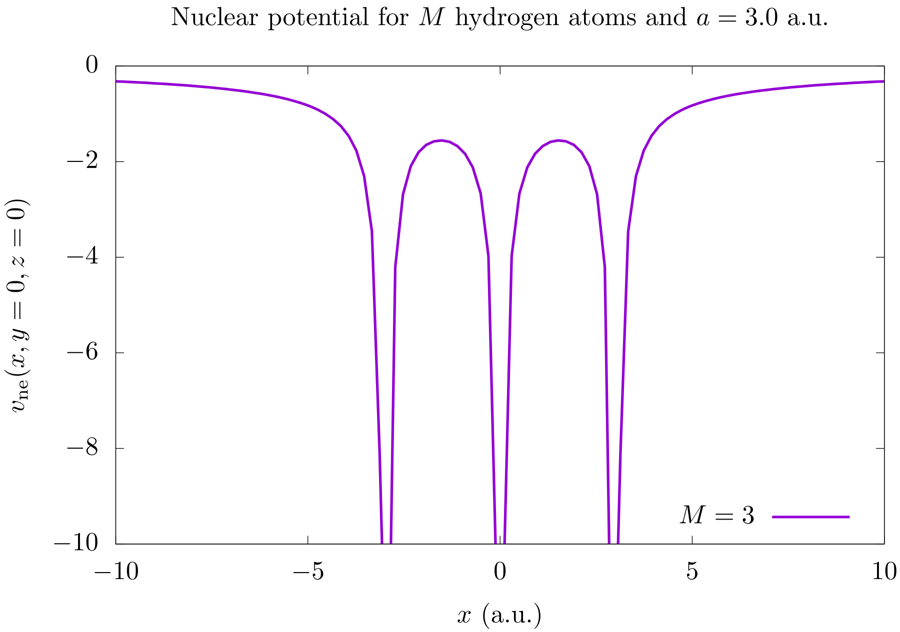
- Nuclear potential energy (in atomic units) for a linear and *periodic* chain of atoms:

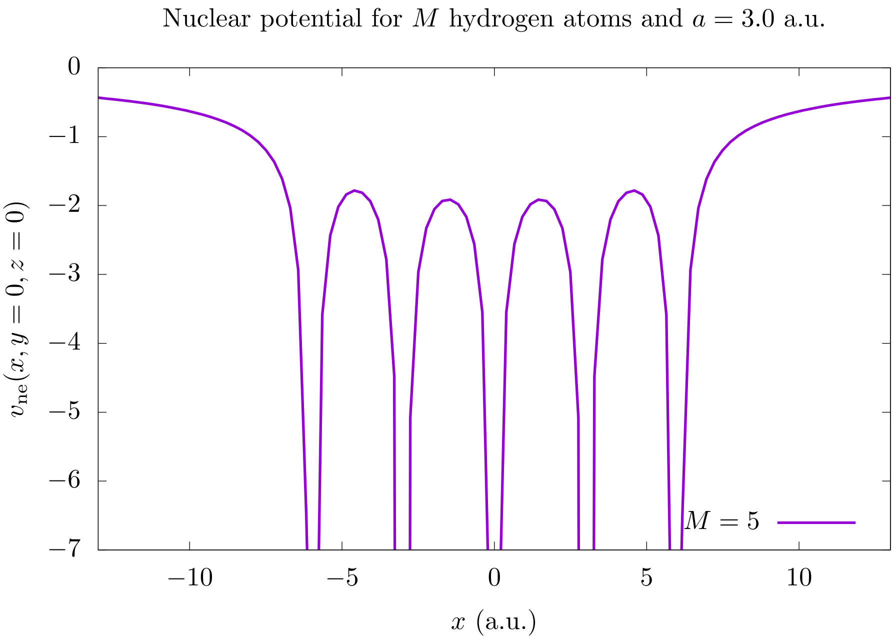
$$v_{\mathrm{ne}}(\mathbf{r}) \equiv v_{\mathrm{ne}}(x,y,z) = -\sum_{n\in\mathbb{Z}} \frac{Z}{\sqrt{(x-na)^2+y^2+z^2}} = v_{\mathrm{ne}}(x+a,y,z)$$

where $\mathbb{Z} = \{0, \pm 1, \pm 2, \ldots\}$ and a is the *lattice constant*.

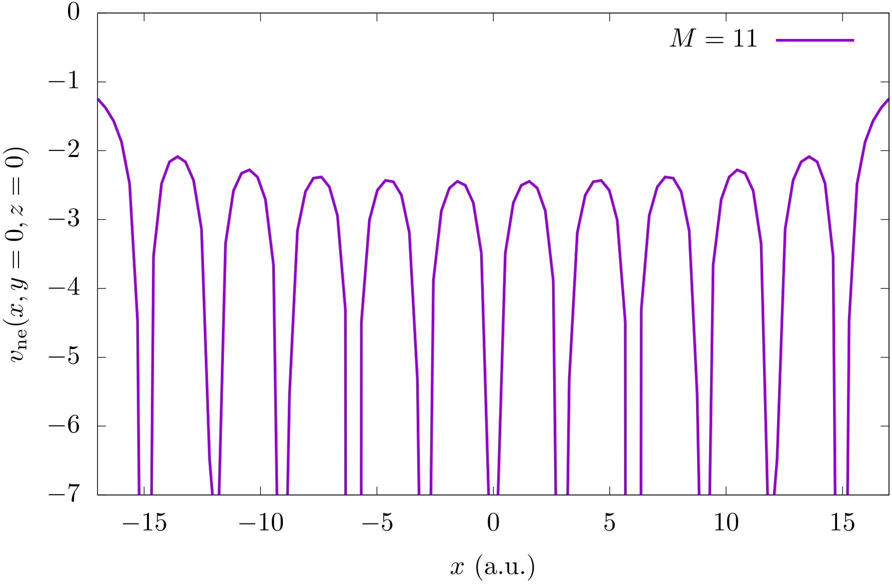
- For simplicity, we will consider a chain of hydrogen atoms ($Z = 1$) in the following.


Nuclear potential for M hydrogen atoms and $a = 3.0$ a.u.
$v_{\rm ne}(x, y = 0, z = 0)$
0
−1
−2
−3
−4
−5
−6
−7
−10
−5
0
5
10
x (a.u.)
$M = 1$

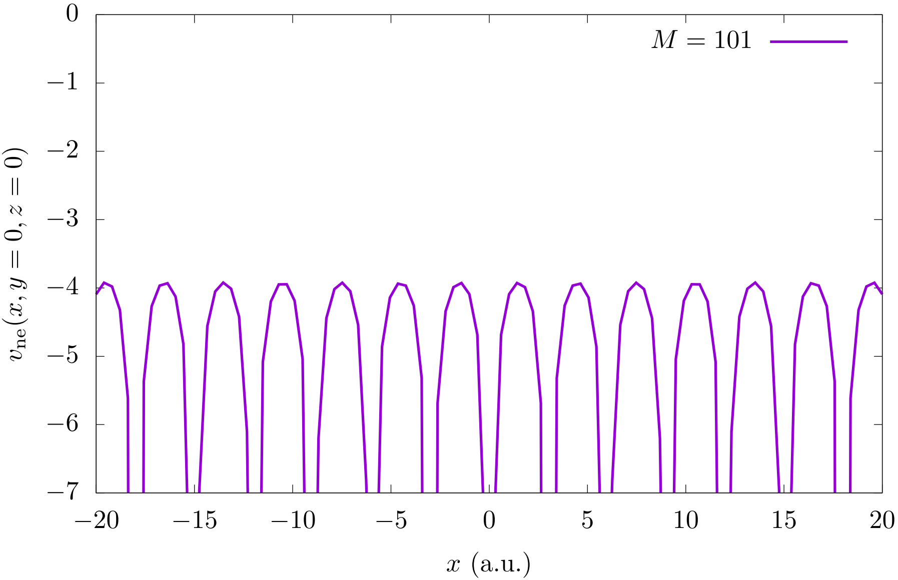

Nuclear potential for M hydrogen atoms and $a = 3.0$ a.u.
$v_{\rm ne}(x, y = 0, z = 0)$
0
−2
−4
−6
−8
−10
−10
−5
0
5
10
x (a.u.)
$M = 3$


Nuclear potential for M hydrogen atoms and $a = 3.0$ a.u.
$v_{\rm ne}(x, y = 0, z = 0)$
x (a.u.)
0
−1
−2
−3
−4
−5
−6
−7
−10
−5
0
5
10
$M = 5$

Nuclear potential for M hydrogen atoms and $a = 3.0$ a.u.



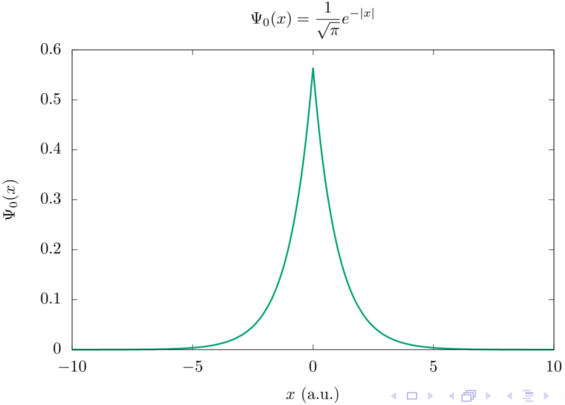
Nuclear potential for M hydrogen atoms and $a = 3.0$ a.u.



The Chemist's approach to periodic systems

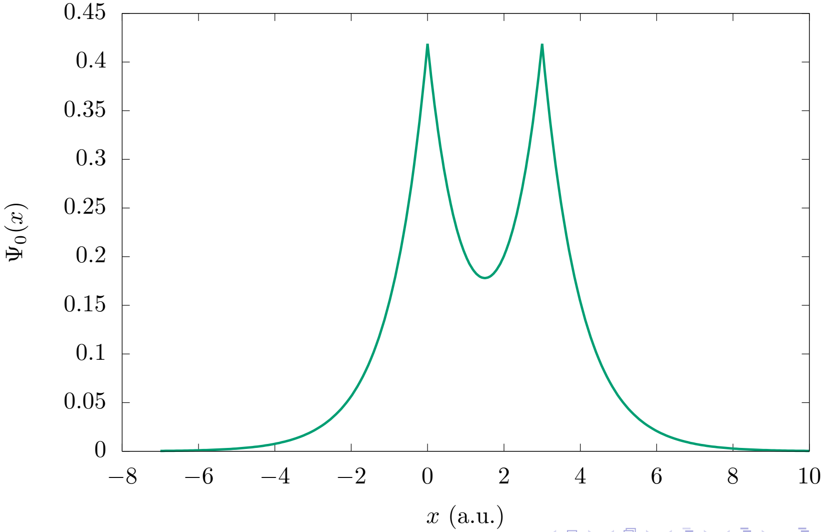
- In order to get some insight into the effect of a periodic nuclear potential on the wavefunction we will (for now) restrict the discussion to *one-electron systems*.

- By analogy with chemistry, we can use, as a starting point, the concept of *linear combination of atomic orbitals* (*LCAO*).
- Let's start with a single atom at position $x = 0$:



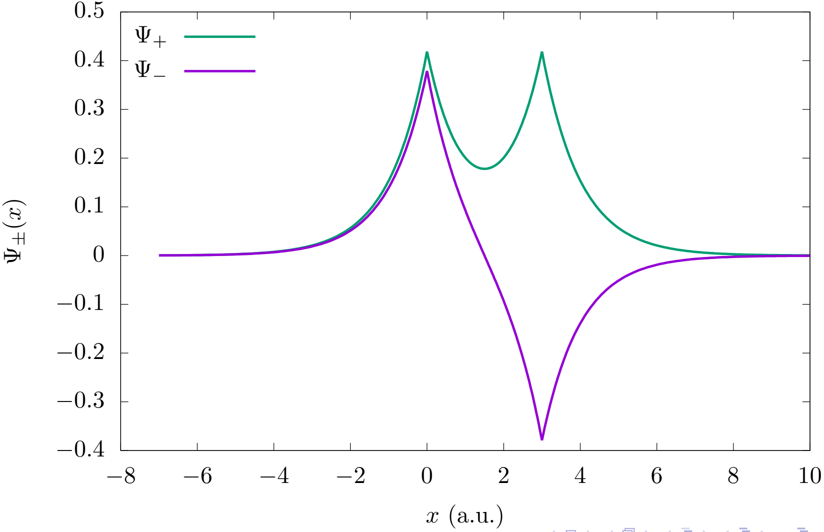
Bonding orbital in the diatomic ($M = 2$)

$$\Psi_0(x) = \frac{1}{\sqrt{2\pi}}\left(e^{-|x|}+e^{-|x-a|}\right) \text{ with } a = 3.0 \text{ a.u.}$$



Bonding/antibonding orbitals in the diatomic ($M = 2$)

$$\Psi_{\pm}(x) = \frac{1}{\sqrt{2\pi}}\left(e^{-|x|} \pm e^{-|x-a|}\right) \text{ with } a = 3.0 \text{ a.u.}$$



Bonding/antibonding densities in the diatomic ($M = 2$)

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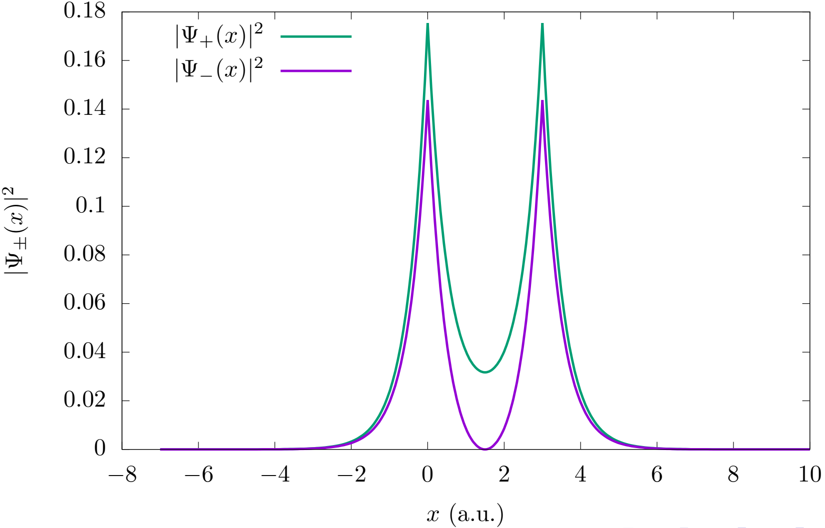
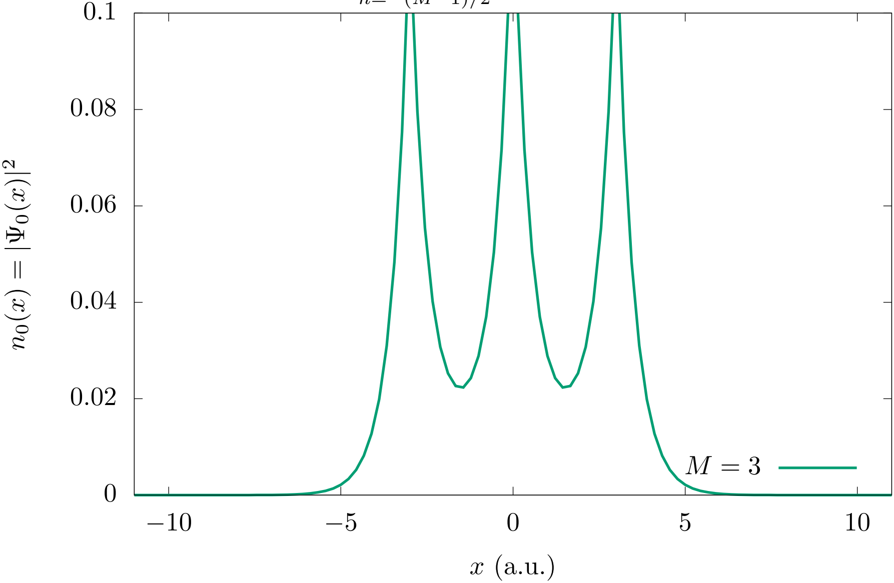
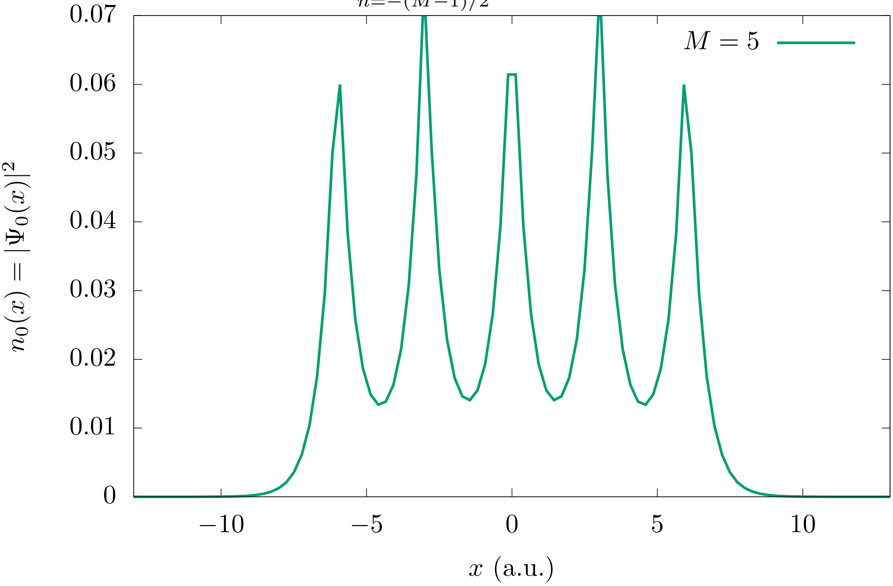


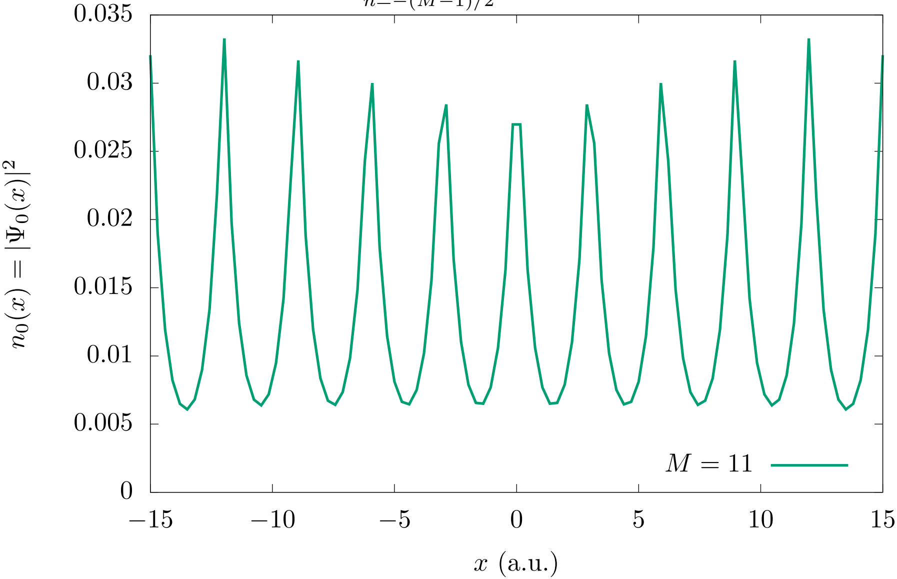
$$\Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n\times a|} \quad \text{where } a = 3.0 \text{ a.u.}$$



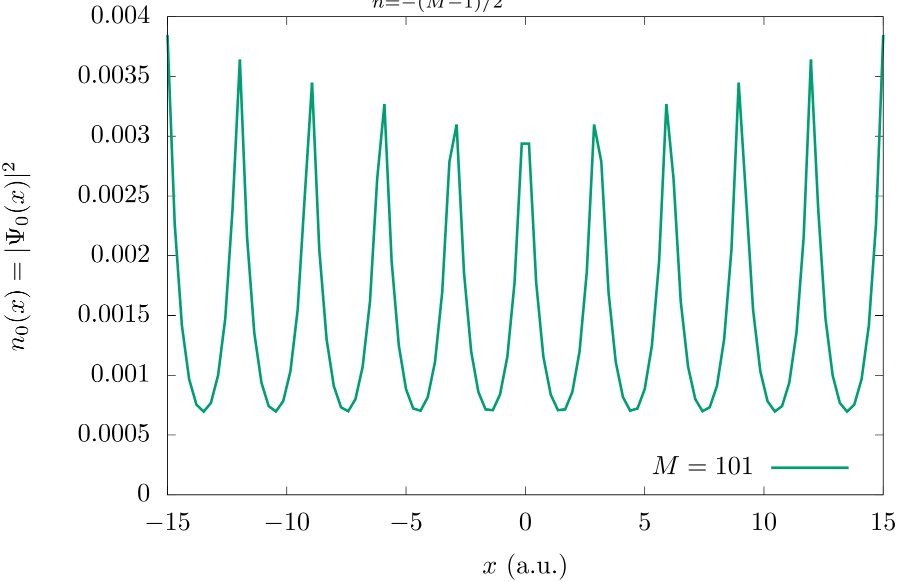
$$\Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n\times a|} \quad \text{where } a = 3.0 \text{ a.u.}$$



$$\Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n\times a|} \quad \text{where } a = 3.0 \text{ a.u.}$$



$$\Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n\times a|} \quad \text{where } a = 3.0 \text{ a.u.}$$



Hückel (or tight-binding) model

- Let us try to rationalize our chemical approach from *first principles*.
- How can we generate (approximate) *solutions* to the Schrödinger equation?
- We can *project* the latter *onto a basis* of (localized) $1s$ atomic orbitals:

$$\phi_n(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-\sqrt{(x-na)^2+y^2+z^2}}$$

- The (one-electron) Hamiltonian matrix elements are

$$h_{nm} = \left\langle \phi_n \middle| \hat{h} \middle| \phi_m \right\rangle = \int \mathrm{d}\mathbf{r}\ \phi_n^*(\mathbf{r}) \times \hat{h}\phi_m(\mathbf{r}),$$

where $\hat{h} \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\mathrm{ne}}(\mathbf{r})\times$.

Hückel (or tight-binding) model

EXERCISE [solution available **here**]

(1) Show that the diagonal elements h_{nn} have the same value (the "α" of Hückel theory).

(2) Show that the matrix elements $h_{n(n+1)}$ between two neighboring $1s$ orbitals have the same value (the "β" of Hückel theory, also denoted "t" or "$-t$").

(3) Show that, if we neglect the overlap between non-neighboring $1s$ orbitals in the calculation of the Hamiltonian matrix elements, then the latter can be written as follows,

$$h_{nm} = \alpha\delta_{nm} + \beta\Big(\delta_{n(m+1)} + \delta_{n(m-1)}\Big)$$

Comment 1: for sake of simplicity, the *overlap* between neighboring orbitals is usually *neglected* when diagonalizing the one-electron Hamiltonian matrix. In other words, the orbital basis is assumed to be orthonormal.

Comment 2: α and β are often used as *parameters*. They might be optimized in order to reproduce experimental data. In the latter case, they will also simulate (some part of) the effect of the two-electron repulsion.

From 3D to 1D

- Let us now return to the *exact* one-electron Schrödinger equation:

$$-\frac{1}{2}\nabla^2_{\mathbf{r}}\Psi(\mathbf{r}) + v_{\rm ne}(\mathbf{r}) \times \Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

- The potential exhibits periodicity along the x axis (symmetry property):

$$v_{\rm ne}(x+a, y, z) = v_{\rm ne}(x, y, z)$$

- We would like to transform the initial three-dimensional problem into the following *one-dimensional* one,

$$\boxed{\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + v(x)\times\right]\varphi(x) = \varepsilon\varphi(x)}$$

where $v(x+a) = v(x)$.

From 3D to 1D

EXERCISE

Let us consider the *exact* wavefunction separation

$$\Psi(\mathbf{r}) \equiv \Psi(x,y,z) = \varphi_{yz}(x) \times \chi(x,y,z),$$

where the wavefunction $\varphi_{yz}(x)$, which is *parameterized* by the coordinates y and z, fulfills the following *one-dimensional* Schrödinger equation,

$$\boxed{\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + v_{yz}(x)\times\right]\varphi_{yz}(x) = \varepsilon_{yz}\varphi_{yz}(x)} \quad \text{with} \quad v_{yz}(x) = v_{\mathrm{ne}}(x,y,z).$$

Note that the above equation describes a one-dimensional periodic problem since $v_{yz}(x+a) = v_{yz}(x)$.

From 3D to 1D

(1) Show that the complementary wavefunction χ fulfills

$$\left(-\frac{1}{2}\frac{\partial^2\chi(x,y,z)}{\partial x^2}+\frac{1}{\varphi_{yz}(x)}\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2}-\frac{1}{2}\frac{\partial^2}{\partial z^2}\right]\Big(\varphi_{yz}(x)\chi(x,y,z)\Big)\right.$$
$$\left.-\frac{1}{\varphi_{yz}(x)}\frac{\partial\varphi_{yz}(x)}{\partial x}\frac{\partial\chi(x,y,z)}{\partial x}\right)+\varepsilon_{yz}\times\chi(x,y,z)=E\chi(x,y,z).$$

(2) Show that, if *(i)* we neglect the variation in both y and z of φ_{yz}, and *(ii)* χ does not vary with x, then the above equation becomes

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2}-\frac{1}{2}\frac{\partial^2}{\partial z^2}\right]\chi(y,z)+\varepsilon_{yz}\times\chi(y,z)\approx E\chi(y,z).$$

Periodicity in the wavefunction

- Our task is now to solve

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+v(x)\times\right]\varphi(x)=\varepsilon\varphi(x) \qquad \text{where} \quad v(x+a)=v(x).$$

- Let us warm up with the *free particle* problem $[v(x)=0]$:

(i) the solution reads $\varphi(x)=C_\varphi\, e^{\mathrm{i}kx}$ and its energy $\varepsilon(k)=k^2/2$ is a *function* of k.

(ii) Note that $\dfrac{1}{\dfrac{\mathrm{d}^2\varepsilon(k)}{\mathrm{d}k^2}}=1$ is the *mass of the electron* in atomic units*.

(iii) The variation of $\varepsilon(k)$ with k, which will be modified by the nuclear potential, is referred to as the *dispersion relation*.

* In SI units, $\varepsilon(k)=\dfrac{\hbar^2k^2}{2m_\mathrm{e}}$ thus leading to $m_\mathrm{e}^{-1}=\dfrac{1}{\hbar^2}\dfrac{\mathrm{d}^2\varepsilon(k)}{\mathrm{d}k^2}$.

Periodicity in the wavefunction

- In the presence of the atoms the wavefunction will have the more general form

$$\varphi(x) = \int_{-\infty}^{+\infty} \mathrm{d}k \; C_\varphi(k) \, e^{\mathrm{i}kx}$$

- The function $C_\varphi(k)$ is the *Fourier transform* of the wavefunction φ.

$\boxed{\textbf{Maths:}}$ Note that $\varphi(x) = 0 \;\; \forall x \quad \Leftrightarrow \quad C_\varphi(k) = 0 \;\; \forall k.$

Periodicity in the wavefunction

EXERCISE [partial solution available **here**]

Let us introduce the Fourier transform of the nuclear potential:

$$v(x) = \int_{-\infty}^{+\infty} \mathrm{d}k \; C_v(k) \, e^{\mathrm{i}kx}$$

(1) Show that the periodicity condition, $v(x + a) = v(x) \;\; \forall x$, implies

$$C_v(k)\left(1 - e^{\mathrm{i}ka}\right) = 0 \;\; \forall k.$$

(2) Deduce that the potential can be written as

$$\boxed{v(x) = \sum_{K \in \frac{2\pi}{a}\mathbb{Z}} V_K \, e^{\mathrm{i}Kx}} \equiv \sum_{m=-\infty}^{+\infty} C_v\left(\frac{2\pi m}{a}\right) e^{\mathrm{i}\frac{2\pi m}{a}x}.$$

The ensemble of K values is called the *reciprocal lattice space*.

Periodicity in the wavefunction

(3) Show, from the Fourier transform expressions of the potential and the wavefunction, that the Schrödinger equation can be rewritten as follows

$$\left(\frac{k^2}{2}-\varepsilon\right)C_\varphi(k)+\sum_{K\in\frac{2\pi}{a}\mathbb{Z}} V_K\, C_\varphi(k-K)=0,\qquad \forall k \tag{1}$$

or, equivalently $(k\rightarrow k-K')$,

$$\left(\frac{(k-K')^2}{2}-\varepsilon\right)C_\varphi(k-K')+\sum_{K"\in\frac{2\pi}{a}\mathbb{Z}} V_{(K"-K')}\, C_\varphi(k-K")=0,\qquad \forall k,\ \ \forall K' \tag{2}$$

(4) Check that the free-particle solutions are recovered from Eq. (1).

Periodicity in the wavefunction

(5) Show that, if Eq. (2) is solved for a *given and fixed* k value, it becomes equivalent to the following diagonalization problem

$$\mathbf{H}(k)\mathbf{X}(k) = \varepsilon(k)\mathbf{X}(k) \tag{3}$$

where

$$\begin{aligned}\mathbf{X}(k) &\equiv X_{K'}(k) = C_{\varphi}(k - K') \\ \mathbf{H}(k) &\equiv H_{K'K"}(k) = \frac{(k - K')^2}{2}\delta_{K'K"} + V_{(K" - K')}\end{aligned}$$

(6) Eq. (3) has in principle an infinite number of solutions $\left\{\mathbf{X}^{(n)}(k)\right\}_n$ with the corresponding energies $\left\{\varepsilon^{(n)}(k)\right\}_n$ where n is a quantum number. Show that the corresponding wavefunction reads

$$\varphi^{(n)}(k, x) = \sum_{K' \in \frac{2\pi}{a}\mathbb{Z}} C_{\varphi}^{(n)}(k - K')e^{\mathrm{i}(k - K')x} \tag{4}$$

Interlude on the first Brillouin zone

$$\boxed{\varphi^{(n)}(k,x)=\sum_{K'\in\frac{2\pi}{a}\mathbb{Z}}C_{\varphi}^{(n)}(k-K')e^{\mathrm{i}(k-K')x}}$$

Note that

$$\begin{aligned}\varphi^{(n)}\left(\boxed{k+\frac{2\pi}{a}},x\right)&=\sum_{K"\in\left(\frac{2\pi}{a}\mathbb{Z}-\frac{2\pi}{a}\right)}C_{\varphi}^{(n)}(k-K")e^{\mathrm{i}(k-K")x}\\&=\sum_{K'\in\frac{2\pi}{a}\mathbb{Z}}C_{\varphi}^{(n)}(k-K')e^{\mathrm{i}(k-K')x}\\&=\varphi^{(n)}(\boxed{k},x).\end{aligned}\tag{5}$$

Conclusion: The solutions to the k-dependent Schrödinger equation (3) are periodic in k with the period $\frac{2\pi}{a}$. Therefore we only need to solve Eq. (3) for k values that belong to an interval of length $\frac{2\pi}{a}$. We usually consider the range $-\frac{\pi}{a}<k\leq+\frac{\pi}{a}$, which is referred to as the *first Brillouin zone*.

Periodicity in the wavefunction

(7) Bloch's theorem states that the wavefunction can be written as follows,

$$\boxed{\varphi^{(n)}(k,x) = e^{\mathrm{i}kx} \times u^{(n)}(k,x)}$$

where $u^{(n)}(k,x+a) = u^{(n)}(k,x)$ ← *periodicity of the lattice!*

Show that this theorem is indeed recovered from Eq. (4).

Let us recall our chemical approach:

$$u^{(n)}(k,x) \longleftarrow \lim_{M\rightarrow+\infty}\left(\frac{1}{\sqrt{\pi M}}\sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n\times a|}\right)$$

$e^{\mathrm{i}kx} \xrightarrow{k=0} +1$ for *any* x **(bonding!)**

$e^{\mathrm{i}kx} \xrightarrow{k=\frac{\pi}{a}} +1$ for $x=0$ and -1 for $x=a$ **(antibonding!)**

Periodicity of the density

$$\boxed{\varphi^{(n)}(k,x) = e^{\mathrm{i}kx} \times u^{(n)}(k,x)}$$

Note that, *unlike the wave function*, the *density* has the *periodicity of the lattice:*

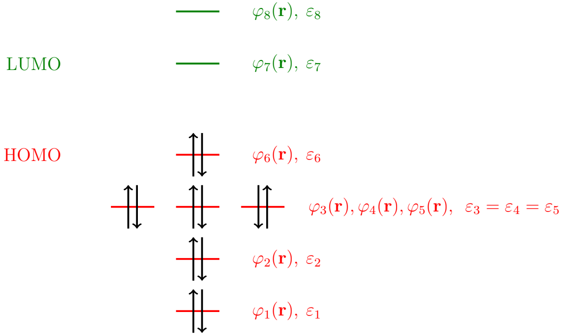
$$\left|\varphi^{(n)}(k,x)\right|^2 = \left|e^{\mathrm{i}kx}\right|^2 \times \left|u^{(n)}(k,x)\right|^2 = \left|u^{(n)}(k,x)\right|^2,$$

so that

$$\left|\varphi^{(n)}(k,x+a)\right|^2 = \left|u^{(n)}(k,x+a)\right|^2 = \left|u^{(n)}(k,x)\right|^2 = \left|\varphi^{(n)}(k,x)\right|^2.$$

One-electron picture of the *many-electron* problem

- The one-electron picture consists in *(i)* calculating the energy levels of a *single electron* and *(ii)* distributing all the electrons among them (*Aufbau principle*).



$\varphi_8(\mathbf{r}),\ \varepsilon_8$

LUMO $\varphi_7(\mathbf{r}),\ \varepsilon_7$

HOMO $\varphi_6(\mathbf{r}),\ \varepsilon_6$

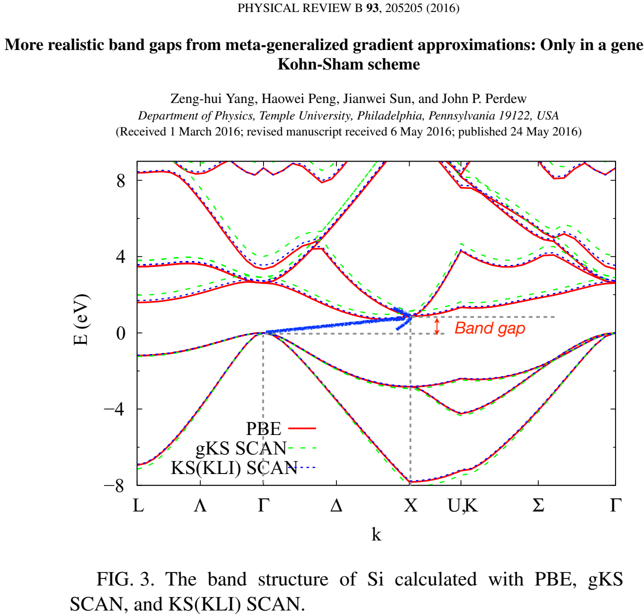
$\varphi_3(\mathbf{r}), \varphi_4(\mathbf{r}), \varphi_5(\mathbf{r}),\quad \varepsilon_3 = \varepsilon_4 = \varepsilon_5$

$\varphi_2(\mathbf{r}),\ \varepsilon_2$

$\varphi_1(\mathbf{r}),\ \varepsilon_1$

- As you know, this picture does *not* give an exact description of the true electronic structure because of the two-electron repulsion. It becomes *formally exact in Kohn–Sham DFT* as, in this case, the one-electron picture *reproduces the exact ground-state density*.

Concept of band structure



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More realistic band gaps from meta-generalized gradient approximations: Only in a generalized Kohn-Sham scheme

Zeng-hui Yang, Haowei Peng, Jianwei Sun, and John P. Perdew
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(Received 1 March 2016; revised manuscript received 6 May 2016; published 24 May 2016)

FIG. 3. The band structure of Si calculated with PBE, gKS SCAN, and KS(KLI) SCAN.

Simplification of the *many-electron* problem

- The exact ground-state electronic structure is in principle described by a *many-electron wavefunction* $\Psi_0\left(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N\right)$.

- When it comes to describe an *extended system*, where the number of electrons N *may go to infinity*, it is natural to wonder if the *wave function* is actually a well defined and reachable mathematical object.

- From a practical point of view, this is for sure *not the way to go*.

- State-of-the-art methods in condensed matter physics do not rely on many-electron wavefunctions.

- They use *reduced* quantities instead.

- The most famous one (in the physics community) is the time-ordered one-electron *Green function* $G(\mathbf{x}, t_1; \mathbf{x}', t_2)$.

- Another important (and simpler) quantity is the electron *density*

$$n(\mathbf{r}) = -\mathrm{i} \sum_{\sigma=\pm\frac{1}{2}} \lim_{t_2\rightarrow t_1, t_1<t_2} G(\mathbf{x}, t_1; \mathbf{x}, t_2), \quad \text{where} \quad \mathbf{x} \equiv (\mathbf{r}, \sigma).$$

- The latter is the basic variable in *density-functional theory*.

The time-ordered one-electron Green function

$$G(\mathbf{x}, t_1; \mathbf{x}', t_2) =$$

The time-ordered one-electron Green function

$$G(\mathbf{x}, t_1; \mathbf{x}', t_2) = \xrightarrow{t_1 > t_2} -\mathrm{i}\langle \Psi_0 | \hat{\Psi}(\mathbf{x}, t_1)\hat{\Psi}^{\dagger}(\mathbf{x}', t_2) | \Psi_0 \rangle$$

The time-ordered one-electron Green function

$\mathrm{i}^2 = -1$

$$-\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^\dagger(\mathbf{x}',t_2)|\Psi_0\rangle$$

$t_1 > t_2$

$$G(\mathbf{x},t_1;\mathbf{x}',t_2) =$$

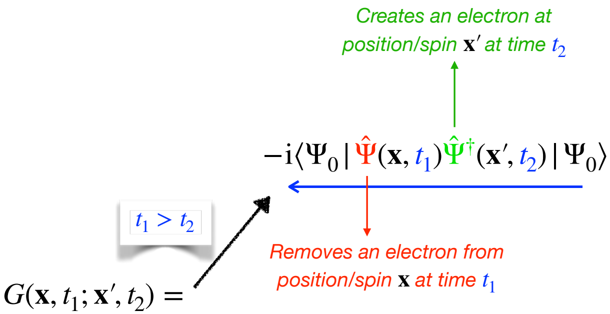
The time-ordered one-electron Green function

Creates an electron at position/spin $\mathbf{x}'$ *at time* t_2

$$G(\mathbf{x},t_1;\mathbf{x}',t_2) \overset{t_1 > t_2}{=} -\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^{\dagger}(\mathbf{x}',t_2)|\Psi_0\rangle$$

Removes an electron from position/spin $\mathbf{x}$ *at time* t_1

The time-ordered one-electron Green function



Creates an electron at position/spin $\mathbf{x}'$ *at time* t_2

$$G(\mathbf{x},t_1;\mathbf{x}',t_2) = -\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^\dagger(\mathbf{x}',t_2)|\Psi_0\rangle$$

$t_1 > t_2$

Removes an electron from position/spin $\mathbf{x}$ *at time* t_1

The time-ordered one-electron Green function

Creates an electron at position/spin $\mathbf{x}'$ *at time* t_2

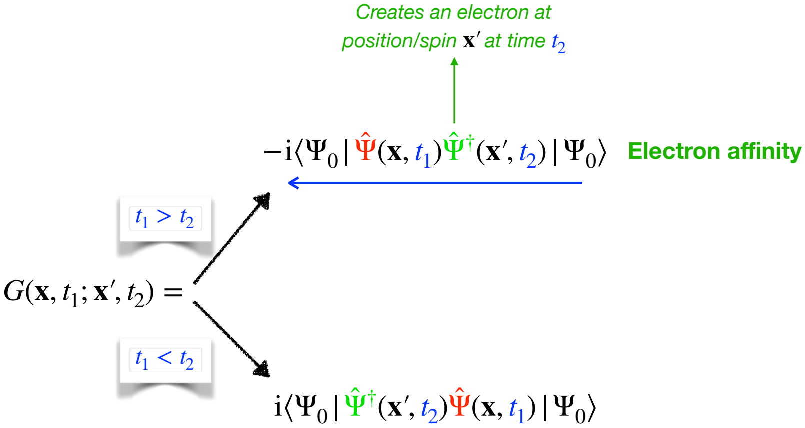
$$-\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^\dagger(\mathbf{x}',t_2)|\Psi_0\rangle$$

Electron affinity

$t_1 > t_2$

$$G(\mathbf{x},t_1;\mathbf{x}',t_2) =$$

The time-ordered one-electron Green function

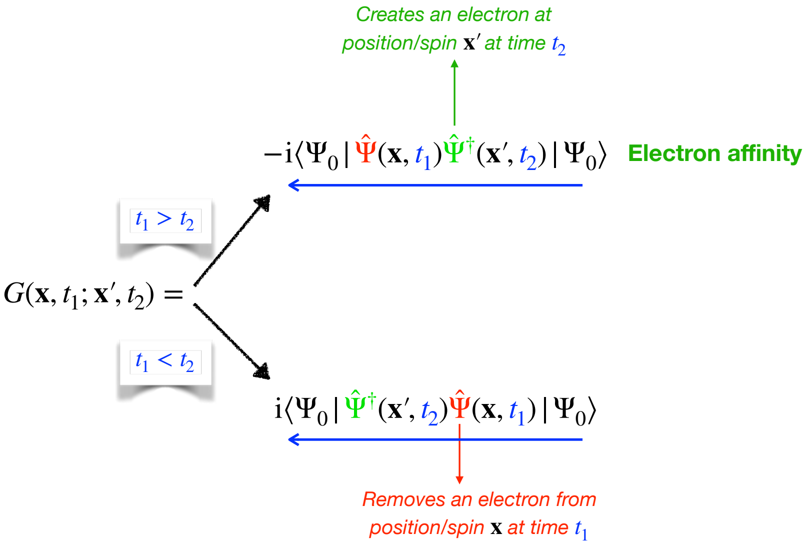


Creates an electron at position/spin $\mathbf{x}'$ *at time* t_2

Electron affinity

$$G(\mathbf{x},t_1;\mathbf{x}',t_2) = \begin{cases} -\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^\dagger(\mathbf{x}',t_2)|\Psi_0\rangle & t_1 > t_2 \\ \mathrm{i}\langle\Psi_0|\hat{\Psi}^\dagger(\mathbf{x}',t_2)\hat{\Psi}(\mathbf{x},t_1)|\Psi_0\rangle & t_1 < t_2 \end{cases}$$

The time-ordered one-electron Green function



Creates an electron at position/spin $\mathbf{x}'$ *at time* t_2

$$-\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^\dagger(\mathbf{x}',t_2)|\Psi_0\rangle$$

Electron affinity

$t_1 > t_2$

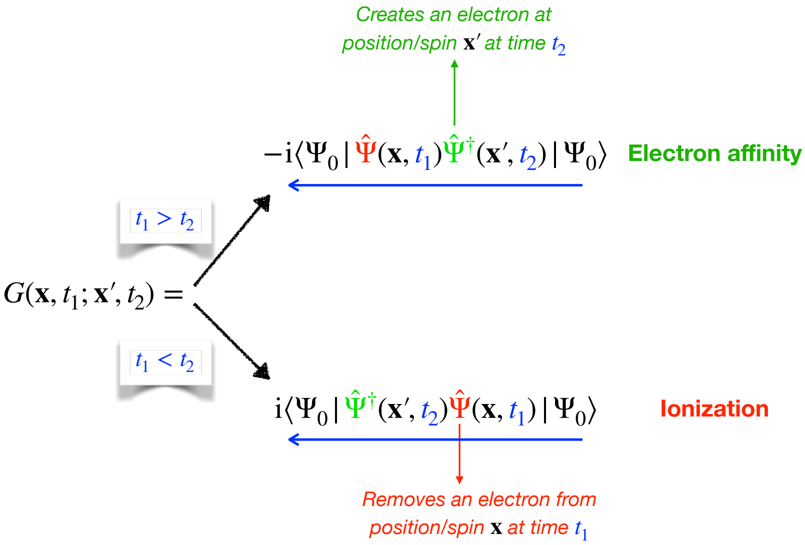
$$G(\mathbf{x},t_1;\mathbf{x}',t_2) =$$

$t_1 < t_2$

$$\mathrm{i}\langle\Psi_0|\hat{\Psi}^\dagger(\mathbf{x}',t_2)\hat{\Psi}(\mathbf{x},t_1)|\Psi_0\rangle$$

Removes an electron from position/spin $\mathbf{x}$ *at time* t_1

The time-ordered one-electron Green function



Creates an electron at position/spin $\mathbf{x}'$ *at time* t_2

$$-\mathrm{i}\langle\Psi_0|\hat{\Psi}(\mathbf{x},t_1)\hat{\Psi}^\dagger(\mathbf{x}',t_2)|\Psi_0\rangle$$

Electron affinity

$t_1 > t_2$

$$G(\mathbf{x},t_1;\mathbf{x}',t_2) =$$

$t_1 < t_2$

$$\mathrm{i}\langle\Psi_0|\hat{\Psi}^\dagger(\mathbf{x}',t_2)\hat{\Psi}(\mathbf{x},t_1)|\Psi_0\rangle$$

Ionization

Removes an electron from position/spin $\mathbf{x}$ *at time* t_1

The time-ordered one-electron Green function

If $\mathbf{x} = \mathbf{x}' \ldots$

$$G(\mathbf{x}, t_1; \mathbf{x}, t_2) =$$

$$\boxed{t_2 \xrightarrow{t_2 > t_1} t_1}$$

$$\mathrm{i}\langle \Psi_0 | \hat{\Psi}^\dagger(\mathbf{x}, t_1)\hat{\Psi}(\mathbf{x}, t_1) | \Psi_0 \rangle$$

The time-ordered one-electron Green function

$$G(\mathbf{x},t_1;\mathbf{x},t_2) =$$

$$\boxed{t_2 \xrightarrow{t_2>t_1} t_1}$$

$$\mathrm{i}\langle\Psi_0|\hat{\Psi}^\dagger(\mathbf{x},t_1)\hat{\Psi}(\mathbf{x},t_1)|\Psi_0\rangle = \mathrm{i}\,n(\mathbf{x})$$

Density!