

Selected Solved Problems on Quantum Mechanics and Solid State Physics

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Abstract

The author had selected and worked out these problems by himself. These problems mainly focus on quantum mechanics, solid state physics and computational physics. It can be regarded as a reference for the graduate students, especially those students in condensed matter physics.

1 Quantum Mechanics

1. Use the variational method to estimate the energy of the ground state of a one-dimensional harmonic oscillator by making use of the two following trial functions: **(a)** $\psi(x, \alpha) = Ae^{-\alpha|x|}$, **(b)** $\psi(x, \alpha) = A(x^2 + \alpha)^{-1}$, where α is a positive real number and where A is the normalization constant.

Solution

(a) According to normalization condition, A should satisfy

$$\int_{-\infty}^{+\infty} \psi^* \psi dx = 2 \int_0^{+\infty} A^2 e^{-2\alpha x} dx = 1$$
$$A^2 = \alpha$$

The first derivative of the trial function $\psi(x, \alpha) = Ae^{-\alpha|x|}$ is discontinuous at $x=0$, so be careful when using the expression $\langle T \rangle = \langle \psi | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} | \psi \rangle = -\frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \psi^* \frac{d^2}{dx^2} \psi dx$. A straightforward, careless use of this expression leads to a negative kinetic energy expectation. Compared with function whose first derivative is continuous, the given trial function lacks some ‘concave part’ due to the discontinuity, which consequently results in the lost of positive kinetic energy. One might instead consider using the following form $\langle T \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx$.

According to the above analysis, kinetic energy equals to

$$\langle T \rangle = \frac{\hbar^2}{2m} \cdot 2 \int_0^{+\infty} A^2 \alpha^2 e^{-2\alpha x} dx = \frac{\hbar^2 \alpha^2}{2m}$$

Actually, kinetic energy can also be calculated via second derivative of the given function correctly, as long as adding the positive contribution of the ‘missing concave part’ through delta function. Therefore,

$$\langle T \rangle = -\frac{\hbar^2}{2m} \left(\int_{-\infty}^{0^-} A^2 \alpha^2 e^{2\alpha x} dx + \int_{0^-}^{0^+} Ae^{\alpha x} \cdot -2A\alpha \delta(x) dx + \int_{0^+}^{+\infty} A^2 \alpha^2 e^{-2\alpha x} dx \right) = \frac{\hbar^2 \alpha^2}{2m}$$

The potential energy for the given function is $\langle U \rangle = \langle \psi | \frac{1}{2} m \omega^2 x^2 | \psi \rangle = \int_{-\infty}^{+\infty} \frac{1}{2} m \omega^2 x^2 \psi^* \psi dx$.

For $a > 0$ and n is a natural number,

$$\int_0^{+\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}.$$

Hence,

$$\langle U \rangle = \int_0^{+\infty} m\omega^2 x^2 A^2 e^{-2\alpha x} dx = \frac{m\omega^2 A^2}{4\alpha^3} = \frac{m\omega^2}{4\alpha^2}.$$

The energy of ψ equals to

$$E = \langle T \rangle + \langle U \rangle = \frac{\hbar^2 \alpha^2}{2m} + \frac{m\omega^2}{4\alpha^2}.$$

Vary the adjustable parameter α to search for the minimum of energy E ,

$$\frac{\partial E}{\partial \alpha} = 0$$

so E has the minimum $\frac{\sqrt{2}}{2}\hbar\omega$ when $\alpha^2 = \frac{\sqrt{2}m\omega}{2\hbar}$, and the upper limit of ground state energy should be $\frac{\sqrt{2}}{2}\hbar\omega$.

(b) From normalization condition, A meets the requirement

$$\int_{-\infty}^{+\infty} \frac{A^2}{(x^2 + \alpha)^2} dx = 1.$$

Next let $x = \sqrt{\alpha} \tan \beta$, therefore

$$\begin{aligned} \int_{-\infty}^{+\infty} \frac{A^2}{(x^2 + \alpha)^2} dx &= \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{A^2}{\alpha^{3/2} \sec^2 \beta} d\beta = \frac{A^2 \pi}{2\alpha^{3/2}} = 1 \\ A^2 &= \frac{2\alpha^{3/2}}{\pi}. \end{aligned}$$

Similarly, the kinetic energy is

$$\langle T \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx = \frac{\hbar^2}{2m} \cdot 4A^2 \int_{-\infty}^{+\infty} \frac{x^2}{(x^2 + \alpha)^4} dx.$$

Replace the variable x again by using $x = \sqrt{\alpha} \tan \beta$, therefore

$$\langle T \rangle = \frac{2A^2 \hbar^2}{m} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{\tan^2 \beta}{\alpha^{5/2} \sec^6 \beta} d\beta = \frac{2A^2 \hbar^2}{m\alpha^{5/2}} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} (1 - \cos^2 \beta) \cos^4 \beta d\beta$$

For an even number n , it can be proved that

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^n \beta d\beta = \frac{n-1}{n} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^{n-2} \beta d\beta,$$

so that

$$\langle T \rangle = \frac{\hbar^2}{4m\alpha}.$$

The potential energy of the trial function equals to

$$\langle U \rangle = \frac{m\omega^2 A^2}{2} \int_{-\infty}^{+\infty} \frac{x^2}{(x^2 + \alpha)^2} dx = \frac{m\omega^2 \alpha}{2}.$$

The minimum of E is $\frac{\sqrt{2}}{2}\hbar\omega$, so the upper limit of ground state is also $\frac{\sqrt{2}}{2}\hbar\omega$.

Note that for any (arbitrary) trial function $|\psi\rangle$ we choose, the energy $E(\psi)$ is always larger than the exact ground state energy E_0 : $E(\psi) \geq E_0$, the equality holds only when $|\psi\rangle$ is proportional to the true ground state $|\psi_0\rangle$. To prove this, we simply expand the trial function

in terms of the exact eigenstates of \hat{H} : $|\psi\rangle = \sum_n a_n |\phi_n\rangle$, and since $E_0 \leq E_n$ for nondegenerate one-dimensional bound systems, we have

$$E(\psi) = \langle \psi | \hat{H} | \psi \rangle = \sum_n |a_n|^2 E_n \geq \sum_n |a_n|^2 E_0 = E_0.$$

2. Consider the quantum mechanical analog to the classical problem of a ball (mass m) bouncing elastically on the floor.

- What is the potential energy, as a function of height x above the floor?
- Use the variational method to estimate the ground state energy of this particle.
- Use the WKB method to estimate the ground state energy of this particle.
- Compare the results of (a) and (b) with the exact ground state energy $E^{exact} = 1.855 \times \sqrt[3]{mg^2\hbar^2} = \sqrt[3]{6.39 \times mg^2\hbar^2}$.

Solution

(a) The potential energy is

$$V(x) = \begin{cases} +\infty, & x < 0 \\ mgx, & x \geq 0 \end{cases}$$

(b) Suppose that the trial function has the form

$$\psi(x) = \begin{cases} 0, & x < 0 \\ Axe^{-\alpha x}, & x \geq 0 \end{cases}$$

where α is a positive real number. According to normalization condition, A should satisfy

$$\int_{-\infty}^{+\infty} \psi^* \psi dx = \int_0^{+\infty} A^2 x^2 e^{-2\alpha x} dx = 1.$$

Hence, $A = 2\alpha^{3/2}$. The kinetic energy equals to

$$\langle T \rangle = \frac{\hbar^2}{2m} \int_{-\infty}^{+\infty} \frac{d\psi^*}{dx} \frac{d\psi}{dx} dx = \int_0^{+\infty} \frac{\hbar^2 A^2}{2m} (1 - x\alpha)^2 e^{-2\alpha x} dx = \frac{\hbar^2 \alpha^2}{2m}.$$

The potential energy equals to

$$\langle U \rangle = \langle \psi | mgx | \psi \rangle = \int_0^{+\infty} A^2 mgx^3 e^{-2\alpha x} dx = \frac{3mg}{2\alpha}.$$

Vary the adjustable parameter α to search for the minimum of energy E ,

$$\frac{\partial E}{\partial \alpha} = \frac{\partial}{\partial \alpha} (\langle T \rangle + \langle U \rangle) = 0.$$

Therefore, the value of α equals to

$$\alpha = \sqrt[3]{\frac{3m^2g}{2\hbar^2}}$$

Substitute this value to calculate the minimum energy, and the estimation of the ground state energy is

$$E_0 = \frac{9}{4} \sqrt[3]{\frac{2}{3} mg^2 \hbar^2}.$$

(c) Suppose that the energy of the particle is represented as E , hence the height of classical turning point equals to E/mg . Since the given potential well has one rigid wall, the integral should satisfy the following relationship

$$\int_0^{\frac{E}{mg}} p(x) dx = (n + \frac{3}{4})\pi\hbar, n = 0, 1, 2, 3, \dots$$

where $p(x)$ can be represented as

$$p(x) = \sqrt{2m(E - mgx)}.$$

For the ground state, $n = 0$ and E can be denoted as E_0 . Consequently,

$$\int_0^{\frac{E_0}{mg}} \sqrt{2m(E_0 - mgx)} dx = \frac{3}{4}\pi\hbar.$$

So the estimation of ground state energy is

$$E_0 = \sqrt[3]{\frac{81\pi^2}{128} mg^2 \hbar^2}.$$

(d) The ground state energy estimation of variational method is little larger than E^{exact} , while the estimation of WKB method is little smaller than E^{exact} .

3. About how long would it take for a can of beer at room temperature to topple over spontaneously, as a result of quantum tunneling?

Hint: Treat it as a uniform cylinder of mass m , radius R , and height h . As the can tips, let z be the height of the center above its equilibrium position $h/2$. The potential energy is mgz , and it topples when z reaches the critical value $z_0 = \sqrt{R^2 + (h/2)^2} - h/2$. Calculate the tunneling probability for $E = 0$. Use $\tau = \frac{2x_1}{v} e^{2\gamma}$, with the thermal energy $\frac{1}{2}mv^2 = \frac{1}{2}kT$ to estimate the velocity. Put in reasonable numbers, and give your answer in years.

Solution: The factor γ is defined as,

$$\gamma \equiv \frac{1}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V(x) - E)} dx.$$

For $E = 0$ and $V(x) = mgx$, γ equals to

$$\gamma = \frac{1}{\hbar} \int_0^{z_0} \sqrt{2m^2 gx} dx = \frac{2m}{3\hbar} \sqrt{2gz_0^3}.$$

The velocity calculated from the thermal energy is $v = \sqrt{\frac{kT}{m}}$. Combining these results yields the toppling time,

$$\tau = 2z_0 \sqrt{\frac{m}{kT}} e^{\frac{4m}{3\hbar} \sqrt{2gz_0^3}}.$$

Suppose that $R = 0.03m$, $h = 0.16m$, $m = 0.5 \text{ kg}$ and $T = 300K$, the expected topple time should be

$$\tau \approx 10^{10^{30.8898}} \text{ years!}$$

4. For Boson Operators, $[\hat{a}, \hat{a}^\dagger] = 1$, (or for the equivalent simple harmonic oscillator) prove the

following relations:

$$\begin{aligned} [\hat{a}, e^{\alpha \hat{a}^\dagger}] &= \alpha e^{\alpha \hat{a}^\dagger} \quad , \quad e^{-\alpha \hat{a}^\dagger} \hat{a} e^{\alpha \hat{a}^\dagger} = \hat{a} + \alpha \\ e^{-\alpha \hat{a}^\dagger} e^{\beta \hat{a}} e^{\alpha \hat{a}^\dagger} &= e^{\beta \alpha} e^{\beta \hat{a}} \quad , \quad e^{\alpha \hat{a}^\dagger} \hat{a} e^{-\alpha \hat{a}^\dagger} = e^{-\alpha} \hat{a} \end{aligned}$$

where α and β are complex numbers.

Solution

(1) Due to the commutator $[\hat{a}, \hat{a}^\dagger] = 1$, for each $n \geq 1$,

$$[\hat{a}, (\hat{a}^\dagger)^n] = (\hat{a}^\dagger)^{n-1} [\hat{a}, \hat{a}^\dagger] + [\hat{a}, (\hat{a}^\dagger)^{n-1}] \hat{a}^\dagger = (\hat{a}^\dagger)^{n-1} + [\hat{a}, (\hat{a}^\dagger)^{n-1}] \hat{a}^\dagger.$$

This process can be repeated until the power of \hat{a}^\dagger in the commutator is smaller than 1. Therefore,

$$[\hat{a}, (\hat{a}^\dagger)^n] = (\hat{a}^\dagger)^{n-1} + (\hat{a}^\dagger)^{n-1} + [\hat{a}, (\hat{a}^\dagger)^{n-3}] (\hat{a}^\dagger)^2 = (n-1) (\hat{a}^\dagger)^{n-1}.$$

Combining the above commutator with series expansion of exponential function yields

$$[\hat{a}, e^{\alpha \hat{a}^\dagger}] = [\hat{a}, \sum_{i=0}^{\infty} \frac{(\alpha \hat{a}^\dagger)^i}{i!}] = \alpha \sum_{i=1}^{\infty} \frac{(\alpha \hat{a}^\dagger)^{i-1}}{(i-1)!} = \alpha e^{\alpha \hat{a}^\dagger}.$$

(2) The above commutator can be expanded as

$$\hat{a} e^{\alpha \hat{a}^\dagger} - e^{\alpha \hat{a}^\dagger} \hat{a} = \alpha e^{\alpha \hat{a}^\dagger}.$$

Notice that complex number α is commutative with any operator,

$$\hat{a} e^{\alpha \hat{a}^\dagger} = e^{\alpha \hat{a}^\dagger} (\hat{a} + \alpha).$$

Premultiply both sides of the above equation by $e^{-\alpha \hat{a}^\dagger}$, the following relationship can be proved.

$$e^{-\alpha \hat{a}^\dagger} \hat{a} e^{\alpha \hat{a}^\dagger} = \hat{a} + \alpha$$

(3) Suppose that $f = e^{-\alpha \hat{a}^\dagger} e^{\beta \hat{a}} e^{\alpha \hat{a}^\dagger}$. Now taking the derivative of f with respect to β yields

$$\frac{df}{d\beta} = e^{-\alpha \hat{a}^\dagger} \hat{a} e^{\beta \hat{a}} e^{\alpha \hat{a}^\dagger}.$$

Since

$$e^{-\alpha \hat{a}^\dagger} \hat{a} e^{\alpha \hat{a}^\dagger} = \hat{a} + \alpha,$$

postmultiplying both sides of the above equation by $e^{-\alpha \hat{a}^\dagger}$ yields

$$e^{-\alpha \hat{a}^\dagger} \hat{a} = (\hat{a} + \alpha) e^{-\alpha \hat{a}^\dagger}.$$

Substitute this relationship into the previous equation of derivative of f ,

$$\frac{df}{d\beta} = (\hat{a} + \alpha) e^{-\alpha \hat{a}^\dagger} e^{\beta \hat{a}} e^{\alpha \hat{a}^\dagger} = (\hat{a} + \alpha) f.$$

The solution of this differential equation is

$$f = C \cdot e^{\beta(\hat{a} + \alpha)},$$

where C is a constant to be determined by initial condition. For $f=1$ if β takes 0, the value of C equals to 1. Therefore,

$$e^{-\alpha\hat{a}^\dagger} e^{\beta\hat{a}} e^{\alpha\hat{a}^\dagger} = e^{\beta\alpha} e^{\beta\hat{a}}.$$

(4) Let $g = e^{\alpha\hat{a}^\dagger\hat{a}}\hat{a}e^{-\alpha\hat{a}^\dagger\hat{a}}$, the derivative of g with respect to α equals to

$$\frac{dg}{d\alpha} = e^{\alpha\hat{a}^\dagger\hat{a}}[\hat{a}^\dagger\hat{a}, \hat{a}]e^{-\alpha\hat{a}^\dagger\hat{a}}$$

The commutator on the right hand side equals to

$$[\hat{a}^\dagger\hat{a}, \hat{a}] = \hat{a}^\dagger[\hat{a}, \hat{a}] + [\hat{a}^\dagger, \hat{a}]\hat{a} = -\hat{a}$$

Consequently,

$$\begin{aligned}\frac{dg}{d\alpha} &= -g, \\ g &= C' \cdot e^{-\alpha}.\end{aligned}$$

Similarly, $g=\hat{a}$ when α is 0, so the constant C' should be \hat{a} . Therefore,

$$e^{\alpha\hat{a}^\dagger\hat{a}}\hat{a}e^{-\alpha\hat{a}^\dagger\hat{a}} = e^{-\alpha}\hat{a}.$$

5. Derive the following relations for Fermi operators.

$$\begin{aligned}1) \quad e^{-\alpha\hat{a}^\dagger}\hat{a}e^{\alpha\hat{a}^\dagger} &= \hat{a} - \alpha^2\hat{a}^\dagger + \alpha(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}) \\ e^{-\alpha\hat{a}}\hat{a}^\dagger e^{\alpha\hat{a}} &= \hat{a}^\dagger - \alpha^2\hat{a} - \alpha(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}) \\ 2) \quad e^{\alpha\hat{a}^\dagger\hat{a}}\hat{a}e^{-\alpha\hat{a}^\dagger\hat{a}} &= e^{-\alpha}\hat{a}, e^{\alpha\hat{a}^\dagger\hat{a}}\hat{a}^\dagger e^{-\alpha\hat{a}^\dagger\hat{a}} = e^{\alpha}\hat{a}^\dagger\end{aligned}$$

Solution

(1) Due to Pauli exclusion principle, for Fermions, the power of creation operator and annihilation operator will vanish whenever $n > 1$.

$$(\hat{a})^n = \hat{O}, (\hat{a}^\dagger)^n = \hat{O} \quad \text{for all } n > 1$$

Therefore,

$$\begin{aligned}e^{-\alpha\hat{a}^\dagger}\hat{a}e^{\alpha\hat{a}^\dagger} &= (1 - \alpha\hat{a}^\dagger)\hat{a}(1 + \alpha\hat{a}^\dagger) = \hat{a} - \alpha^2\hat{a}^\dagger + \alpha(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a}) \\ e^{-\alpha\hat{a}}\hat{a}^\dagger e^{\alpha\hat{a}} &= (1 - \alpha\hat{a})\hat{a}^\dagger(1 + \alpha\hat{a}) = \hat{a}^\dagger - \alpha^2\hat{a} - \alpha(\hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a})\end{aligned}$$

(2) Let $f = e^{\alpha\hat{a}^\dagger\hat{a}}\hat{a}e^{-\alpha\hat{a}^\dagger\hat{a}}$, then take the derivative of f with respect to α ,

$$\frac{df}{d\alpha} = e^{\alpha\hat{a}^\dagger\hat{a}}(\hat{a}^\dagger\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger\hat{a})e^{-\alpha\hat{a}^\dagger\hat{a}}$$

The anticommutator for Fermions satisfies $[\hat{a}, \hat{a}^\dagger]_+ = 1$. Substituting this anticommutator and $\hat{a}\hat{a} = \hat{O}$ into the equation of derivative yields

$$\frac{df}{d\alpha} = -f.$$

The solution of this differential equation is

$$f = C \cdot e^{-\alpha}.$$

Since $f = \hat{a}$ when $\alpha=0$, C must equal to \hat{a} . Hence

$$e^{\alpha\hat{a}^\dagger\hat{a}}\hat{a}e^{-\alpha\hat{a}^\dagger\hat{a}} = e^{-\alpha}\hat{a}.$$

The last equation can also be proved in a similar way, and reader can have a try.

2 Solid State Physics

1. The primitive translation vectors of fcc Bravais lattice are:

$$\mathbf{a} = \frac{a}{2}(0, 1, 1), \mathbf{b} = \frac{a}{2}(1, 0, 1), \mathbf{c} = \frac{a}{2}(1, 1, 0)$$

where a is the side of the cube.

Show that $\mathbf{G}_1 = \frac{2\pi}{a}(2, 0, 0)$, $\mathbf{G}_2 = \frac{2\pi}{a}(2, 2, 0)$, $\mathbf{G}_3 = \frac{2\pi}{a}(2, 2, 2)$ are allowed vectors of reciprocal lattice, while $\mathbf{G} = \frac{2\pi}{a}(3, 0, 0)$ is not.

Solution

The basis of the reciprocal space of the fcc lattice expressed in the orthogonal basis $(\hat{x}, \hat{y}, \hat{z})$ are,

$$\mathbf{A} = \frac{2\pi}{a}(-1, 1, 1); \mathbf{B} = \frac{2\pi}{a}(1, -1, 1); \mathbf{C} = \frac{2\pi}{a}(1, 1, -1)$$

And the generic reciprocal lattice vector will be

$$\mathbf{G} = k\mathbf{A} + p\mathbf{B} + q\mathbf{C},$$

where k, p, q are integers. In the orthogonal basis, it is normally referred to,

$$\mathbf{G} = \frac{2\pi}{a}[\hat{x}(-k + p + q) + \hat{y}(k - p + q) + \hat{z}(k + p - q)],$$

and we can see that the system

$$\begin{cases} -k + p + q = 3 \\ k - p + q = 0 \\ k + p - q = 0 \end{cases}$$

does not admit solution in the set of integers.

2. Prove that (1) the volume of the primitive cell multiplied the volume of the corresponding reciprocal primitive cell is $(2\pi)^3$; (2) the reciprocal primitive cell has the exactly same point group symmetry as the primitive cell.

Solution

(1) The basis of the reciprocal primitive cell are defined according to the following rules,

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} = \begin{cases} 2\pi & (i = j) \\ 0 & (i \neq j) \end{cases}$$

where $i, j=1, 2, 3$. Denote the volume of the primitive cell with Ω , and that of reciprocal cell with Ω^* . Hence,

$$\mathbf{b}_1 = \frac{2\pi}{\Omega}(\mathbf{a}_2 \times \mathbf{a}_3), \quad \mathbf{b}_2 = \frac{2\pi}{\Omega}(\mathbf{a}_3 \times \mathbf{a}_1), \quad \mathbf{b}_3 = \frac{2\pi}{\Omega}(\mathbf{a}_1 \times \mathbf{a}_2).$$

The volume of reciprocal primitive cell can be worked out through

$$\Omega^* = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \left(\frac{2\pi}{\Omega}\right)^3 (\mathbf{a}_2 \times \mathbf{a}_3) \cdot [(\mathbf{a}_3 \times \mathbf{a}_1) \times (\mathbf{a}_1 \times \mathbf{a}_2)].$$

Since $(\mathbf{a} \times \mathbf{b}) \times \mathbf{c} = (\mathbf{a} \cdot \mathbf{c})\mathbf{b} - (\mathbf{b} \cdot \mathbf{c})\mathbf{a}$,

$$\Omega^* = \left(\frac{2\pi}{\Omega}\right)^3 (\mathbf{a}_2 \times \mathbf{a}_3) \cdot [\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)]\mathbf{a}_1 = \frac{(2\pi)^3}{\Omega}.$$

Therefore, $\Omega \cdot \Omega^* = (2\pi)^3$.

(2) Suppose that α is a symmetrization operation in the primitive point group, therefore $\alpha \mathbf{R}_l$ is still a lattice vector. For each element α in the group, there must exist a reverse element α^{-1} so that $\alpha^{-1} \mathbf{R}_l$ is also a lattice vector. Therefore,

$$\alpha^{-1} \mathbf{R}_l \cdot \mathbf{K}_n = 2\pi m.$$

Since symmetrization operation is orthogonal transformation, which keeps the inner product of two vectors unchanged after transformation, the above equation can be reduced to the following form,

$$\mathbf{R}_l \cdot \alpha \mathbf{K}_n = 2\pi m.$$

Hence, for each element α in the symmetrization group, $\alpha \mathbf{K}_n$ is also a reciprocal lattice vector. The reciprocal lattice shares the same symmetrization group with the primitive lattice.

3. Gold has a face-centered cubic Bravais lattice whose lattice constant $a=4.08\text{\AA}$. The potential energy of the crystal composed of N atoms can be approximately written as $U = \frac{N}{2} \sum_{\mathbf{R}} \varepsilon_b \left[\left(\frac{r_e}{R} \right)^{12} - 2 \left(\frac{r_e}{R} \right)^6 \right]$ (sum of the Lennard-Jones potentials), where ε_b is the binding energy at the distance r_e of the nearest neighbors. \mathbf{R} runs on all vectors of the lattice. Assuming that the contribution to U is only due to the interaction with the nearest neighbors, and that the total binding energy is given by the enthalpy of sublimation $\Delta H_s = 368 \text{ kJ/mole}$, calculate ε_b and, in harmonic approximation, determine the force constant κ and the vibration frequency ω .

(Neglect the kinetic contribution to the total energy of the crystal.)

Solution

Since the lattice is fcc, the closest neighbors are $z=12$ at the equilibrium distance $r_e = \frac{a}{\sqrt{2}} = 2.885\text{\AA}$. Because the sum of U is limited to the nearest neighbors (pv) setting $R = r_e$ yields

$$U_{pv} = -\frac{N}{2} \sum_{pv} \varepsilon_b = -\frac{zN}{2} \varepsilon_b$$

and for one mole atoms $\Delta H_s = \frac{z}{2} N_A \varepsilon_b$, where N_A is the Avogadro constant, from which

$$\varepsilon_b = \frac{\Delta H}{6N_A} = 0.64 \text{ eV/atom}.$$

Expanding the potential energy of each atom to the second order

$$U_{pv}(R) = \frac{z}{2} \varepsilon_b \left[\left(\frac{r_e}{R} \right)^{12} - 2 \left(\frac{r_e}{R} \right)^6 \right],$$

we obtain

$$\left. \frac{d^2 U_{pv}}{dR^2} \right|_{r_e} = 12 \frac{z}{2} \varepsilon_b r_e^6 \left[13 r_e^6 \left(\frac{1}{R} \right)^{14} - 7 \left(\frac{1}{R} \right)^8 \right] \Big|_{r_e} = 432 \frac{\varepsilon_b}{r_e^2},$$

from which

$$\kappa = 33.2 \text{ eV/\AA}^2$$

and

$$\omega = \sqrt{\frac{\kappa}{M_{Au}}} = 4.02 \times 10^{13} \text{ rad} \cdot \text{s}^{-1},$$

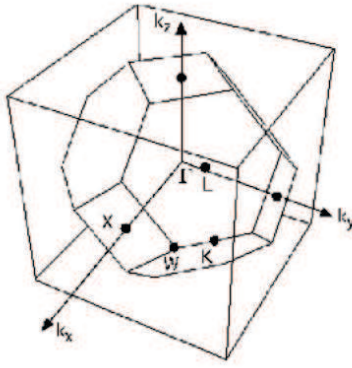


Figure 1: First Brillouin zone of a face-centered cubic lattice

where $M_{Au} = 3.28 \times 10^{-25} \text{ kg/atom}$.

4. Aluminum (Al) is a trivalent fcc metal with lattice parameter $a = 4.04 \text{ \AA}$. Calculate, in the free electron approximation, the energy bands along the ΓX , ΓK and ΓL directions of the first Brillouin zone, where Γ is the center of the zone.

- Describe the bands along these directions of high symmetry.
- Calculate the position of the Fermi level.
- State whether the first Brillouin zone is entirely contained in the Fermi sphere.

Solution

The basis of a fcc in directed space is

$$\mathbf{a} = \frac{a}{2}(1, 0, 1), \mathbf{b} = \frac{a}{2}(1, 1, 0), \mathbf{c} = \frac{a}{2}(0, 1, 1)$$

where a is the side of the cube of the unit cell. The reciprocal basis is obtained from it:

$$\mathbf{A} = \frac{2\pi}{a}(1, -1, 1), \mathbf{B} = \frac{2\pi}{a}(1, 1, -1), \mathbf{C} = \frac{2\pi}{a}(-1, 1, 1).$$

The latter describes a bcc lattice in the reciprocal space whose unit cell is a cube of side length

$$|\mathbf{l}| = \frac{2\pi}{a}|(1, 1, 1) - (1, -1, 1)| = \frac{2\pi}{a}|(020)| = \frac{4\pi}{a}.$$

The first Brillouin zone is represented in the figure 1, from which it is immediate to determine the coordinates of the points X and L:

$$X \equiv \frac{2\pi}{a}(1, 0, 0); L \equiv \frac{2\pi}{a}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right).$$

To determine the coordinates of point K, considering the figure 2, it shows that

$$l = 4 \frac{\sqrt{2}}{2} d = 2\sqrt{2}d.$$

Therefore the projection of point K along the direction XW, from point X, equals to $\frac{d}{2} \frac{\sqrt{2}}{2} + d \frac{\sqrt{2}}{2} = \frac{3}{4}d\sqrt{2} = \frac{3}{8}l$. So the coordinates of point K are

$$K \equiv \frac{2\pi}{a}\left(\frac{3}{4}, \frac{3}{4}, 0\right).$$

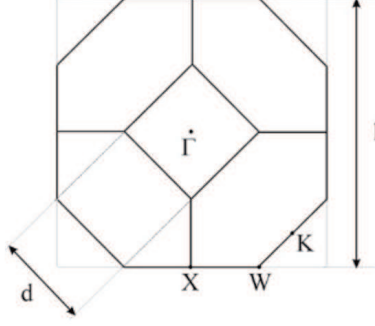


Figure 2: Flat section of the Brillouin zone

Using the form of free electron, it is obtained:

$$E_X = \frac{\hbar^2}{2m} \left(\frac{2\pi}{a} \right)^2 (1 + 0 + 0)^2 = 9.23eV.$$

Similarly E_K and E_L are calculated

$$E_K = 10.4eV \quad \text{and} \quad E_L = 6.9eV.$$

The energy bands are branches of parabola. Considering Pauli exclusion principle and the spin of electron, each reciprocal primitive cell can host two electrons, so that

$$2 \times \frac{V_{Fermi}}{V_{Rep}} = \frac{V k_F^3}{3\pi^2} = N.$$

Furthermore, each aluminium atom has three valent electrons, therefore the Fermi surface is a sphere of radius $k_F^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 \frac{12}{a^3}$ and the Fermi energy is

$$E_F = \frac{\hbar^2 k_F^2}{2m} = (6\pi)^{4/3} \frac{\hbar^2}{2ma^2} = 11.73eV.$$

The point W of the first Brillouin zone is the most distant from the point Γ , and has coordinates $W \equiv \frac{2\pi}{a}(1, \frac{1}{2}, 0)$. Therefore

$$\frac{k_F}{k_W} = \frac{\sqrt[3]{36\pi^2}}{\pi\sqrt{5}} = 1.008,$$

the first Brillouin zone is entirely contained in the Fermi sphere.

3 Computational Physics

1.The overlap matrix S is defined as

$$S_{pq} = \langle \chi_p | \chi_q \rangle .$$

Consider a vector ψ that can be expanded in the basis χ_p as:

$$\psi = \sum_p C_p | \chi_p \rangle .$$

(a) Suppose ψ is normalised. Show that \mathbf{C} then satisfies:

$$\sum_{pq} C_p^* S_{pq} C_q = 1.$$

(b) Show that the eigenvalues of \mathbf{S} are positive.

Solution (a) Since ψ is normalised, $\langle \psi | \psi \rangle = 1$, consequently

$$\left(\sum_p C_p^* \langle \chi_p | \right) \left(\sum_q C_q | \chi_q \rangle \right) = \sum_{pq} C_p^* \langle \chi_p | \chi_q \rangle C_q = \sum_{pq} C_p^* S_{pq} C_q = 1$$

(b) For any vector ψ in the Hilbert space, the inner product of ψ with itself is always greater than 0, $\langle \psi | \psi \rangle > 0$. This inequality can also be expressed as

$$\langle \psi | \psi \rangle = \mathbf{C}^* \mathbf{S} \mathbf{C} > 0.$$

Therefore, \mathbf{S} is a Hermite positive matrix and the eigenvalues of \mathbf{S} are positive.

2. MacDonald's theorem states that, in linear variational calculus, not only the variational ground state but also the higher variational eigenvectors have eigenvalues that are higher than the corresponding eigenvalues of the full problem.

Consider an Hermitian operator \mathcal{H} and its variational matrix representation \mathbf{H} defined by

$$H_{pq} = \langle \chi_p | \mathcal{H} | \chi_q \rangle.$$

χ_p are the basis vectors of the linear variational calculus. They form a finite set.

We shall denote the eigenvectors of \mathcal{H} by ϕ_k and the corresponding eigenvalues by λ_k ; Φ_k are the eigenvectors of \mathbf{H} with eigenvalues Λ_k . They are all ordered, i.e. ϕ_0 corresponds to the lowest eigenvalue and so on, and similarly for the Φ_k .

(a) Write Φ_0 as an expansion in the complete set ϕ_k in order to show that

$$\frac{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = \Lambda_0 \geq \lambda_0.$$

(b) Suppose Φ'_1 is a vector perpendicular to ϕ_0 . Show that

$$\frac{\langle \Phi'_1 | \mathcal{H} | \Phi'_1 \rangle}{\langle \Phi'_1 | \Phi'_1 \rangle} \geq \lambda_1.$$

(Note that, in general, the lowest-but-one variational eigenstate Φ_1 is not perpendicular to ϕ_0 so this result does not guarantee $\Lambda_1 \geq \lambda_1$.)

(c) Consider a vector $\Phi'_1 = \alpha \Psi_0 + \beta \Psi_1$ which is perpendicular to ϕ_0 . From (b) it is clear that $\langle \Phi'_1 | \mathcal{H} | \Phi'_1 \rangle / \langle \Phi'_1 | \Phi'_1 \rangle \geq \lambda_1$. Show that

$$\frac{\langle \Phi'_1 | \mathcal{H} | \Phi'_1 \rangle}{\langle \Phi'_1 | \Phi'_1 \rangle} = \frac{|\alpha|^2 \Lambda_0 + |\beta|^2 \Lambda_1}{|\alpha|^2 + |\beta|^2}.$$

and that from this it follows that $\Lambda_1 \geq \lambda_1$. This result can be generalised for higher states.

Solution (a) Expand Φ_0 in the complete set ϕ_k as the following:

$$\Phi_0 = \sum_k a_k | \phi_k \rangle$$

Due to the orthonormal relationship of the basis, it can be deduced that

$$\frac{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = \frac{\sum_{k=0} \lambda_k |a_k|^2}{\sum_{k=0} |a_k|^2} \geq \frac{\sum_{k=0} \lambda_0 |a_k|^2}{\sum_{k=0} |a_k|^2}.$$

Therefore,

$$\frac{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = \Lambda_0 \geq \lambda_0.$$

(b) Supposed that Φ'_1 has been expanded in the basis as the following:

$$\Phi'_1 = \sum_i a'_i |\phi_i \rangle.$$

Since Φ'_1 is a vector perpendicular to ϕ_0 , the following relationship should be satisfied:

$$\langle \phi_0 | \Phi'_1 \rangle = a'_0 = 0.$$

Consequently,

$$\frac{\langle \Phi'_1 | \mathcal{H} | \Phi'_1 \rangle}{\langle \Phi'_1 | \Phi'_1 \rangle} = \frac{\sum_{i=1} \lambda_i |a_i|^2}{\sum_{i=1} |a_i|^2} \geq \lambda_1.$$

(c) The eigenvectors of \mathbf{H} also satisfy the orthonormal relationship, so

$$\frac{\langle \Phi'_1 | \mathcal{H} | \Phi'_1 \rangle}{\langle \Phi'_1 | \Phi'_1 \rangle} = \frac{|\alpha|^2 \Lambda_0 + |\beta|^2 \Lambda_1}{|\alpha|^2 + |\beta|^2} \geq \lambda_1.$$

From $\Lambda_1 > \Lambda_0$, finally we can conclude that

$$\Lambda_1 \geq \frac{|\alpha|^2 \Lambda_0 + |\beta|^2 \Lambda_1}{|\alpha|^2 + |\beta|^2} \geq \lambda_1,$$

and $\Lambda_1 = \lambda_1$ if and only if $|\alpha|^2 = 0$.

3. For a two-electron system, the wave function can be written as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \Phi(\mathbf{r}_1, \mathbf{r}_2) \cdot \chi(s_1, s_2).$$

Because the wave function Ψ is antisymmetric under particle exchange, we may take Φ symmetric in 1 and 2 and χ antisymmetric, or vice versa.

We construct the functions Ψ and χ from the orthonormal spatial orbitals $\phi_1(\mathbf{r})$, $\phi_2(\mathbf{r})$ and the spin-up and -down functions $\alpha(s)$ and $\beta(s)$ respectively.

(a) Write down the antisymmetric wave functions that can be constructed in this way (there are six of them).

(b) Write down all possible Slater determinants that can be built from the one-electron spin-orbitals consisting of a product of one of the orbitals ϕ_1 and ϕ_2 and a spin-up or -down spinor (you will find six of these determinants too).

(c) Express the wave functions of part (a) of this problem in those of (b).

Solution (a) There are three wavefunctions if we take Φ symmetric and χ antisymmetric.

$$\begin{aligned} \Psi_1 &= \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \cdot \frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)] \\ \Psi_2 &= \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \cdot \frac{1}{\sqrt{2}}[\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)] \\ \Psi_3 &= \frac{1}{2}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)][\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)] \end{aligned}$$

The other three can be found if take Φ antisymmetric and χ symmetric.

$$\begin{aligned}\Psi_4 &= \frac{1}{\sqrt{2}}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)] \cdot \alpha(s_1)\alpha(s_2) \\ \Psi_5 &= \frac{1}{\sqrt{2}}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)] \cdot \beta(s_1)\beta(s_2) \\ \Psi_6 &= \frac{1}{2}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)][\alpha(s_1)\beta(s_2) + \alpha(s_2)\beta(s_1)]\end{aligned}$$

(b) All possible Slater determinants are

$$\begin{aligned}\Psi'_1 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(s_1) & \phi_1(\mathbf{r}_2)\alpha(s_2) \\ \phi_1(\mathbf{r}_1)\beta(s_1) & \phi_1(\mathbf{r}_2)\beta(s_2) \end{vmatrix} \\ \Psi'_2 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(\mathbf{r}_1)\alpha(s_1) & \phi_2(\mathbf{r}_2)\alpha(s_2) \\ \phi_2(\mathbf{r}_1)\beta(s_1) & \phi_2(\mathbf{r}_2)\beta(s_2) \end{vmatrix} \\ \Psi'_3 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(s_1) & \phi_1(\mathbf{r}_2)\alpha(s_2) \\ \phi_2(\mathbf{r}_1)\beta(s_1) & \phi_2(\mathbf{r}_2)\beta(s_2) \end{vmatrix} \\ \Psi'_4 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(s_1) & \phi_1(\mathbf{r}_2)\alpha(s_2) \\ \phi_2(\mathbf{r}_1)\alpha(s_1) & \phi_2(\mathbf{r}_2)\alpha(s_2) \end{vmatrix} \\ \Psi'_5 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\beta(s_1) & \phi_1(\mathbf{r}_2)\beta(s_2) \\ \phi_2(\mathbf{r}_1)\beta(s_1) & \phi_2(\mathbf{r}_2)\beta(s_2) \end{vmatrix} \\ \Psi'_6 &= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_2(\mathbf{r}_1)\alpha(s_1) & \phi_2(\mathbf{r}_2)\alpha(s_2) \\ \phi_1(\mathbf{r}_1)\beta(s_1) & \phi_1(\mathbf{r}_2)\beta(s_2) \end{vmatrix}\end{aligned}$$

(c) Wave functions of part (a) can be easily represented through Slater determinants of part (b) as the followings:

$$\Psi_1 = \Psi'_1, \Psi_2 = \Psi'_2, \Psi_3 = \frac{1}{\sqrt{2}}(\Psi'_3 + \Psi'_6), \Psi_4 = \Psi'_4, \Psi_5 = \Psi'_5, \Psi_6 = \frac{1}{\sqrt{2}}(\Psi'_3 - \Psi'_6).$$

4. Consider the helium atom with two electrons having the same spin, represented by the spinor $\alpha(s)$.

(a) Give the form of the two-electron wave function, expressed in orthonormal spatial orbitals ϕ_1 and ϕ_2 .

(b) Write down the Schrödinger equation for this system.

(c) Give an expression for the expectation value of the energy in the orbitals ϕ_i .

Solution (a) The form of two-electron wave functions can be expressed as,

$$\Psi = \frac{1}{\sqrt{2}}[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)] \cdot \alpha(s_1)\alpha(s_2)$$

(b) The Schrödinger equation for this system is

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \Psi = E\Psi.$$

(c) The expectation value of the energy in the orbitals ϕ_i is

$$E_i = \int d\mathbf{r}_i^3 \phi_i^* \left(-\frac{1}{2} \nabla_i^2 - \frac{2}{r_i} \right) \phi_i + \int d\mathbf{r}_i^3 |\phi_i(\mathbf{r}_i)|^2 \left(\int d\mathbf{r}_1^3 \frac{|\phi_1(\mathbf{r}_1)|^2}{|\mathbf{r}_1 - \mathbf{r}_i|} + \int d\mathbf{r}_2^3 \frac{|\phi_2(\mathbf{r}_2)|^2}{|\mathbf{r}_2 - \mathbf{r}_i|} \right) - \int d\mathbf{r}_i^3 \left(\int d\mathbf{r}_1^3 \frac{\phi_1^*(\mathbf{r}_1) \phi_1(\mathbf{r}_i) \phi_i^*(\mathbf{r}_i) \phi_i(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_i|} + \int d\mathbf{r}_2^3 \frac{\phi_2^*(\mathbf{r}_2) \phi_2(\mathbf{r}_i) \phi_i^*(\mathbf{r}_i) \phi_i(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_i|} \right)$$

5. Consider a Slater determinant

$$\Psi_{AS}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} \sum_{\mathbf{P}} \epsilon_{\mathbf{P}} \mathbf{P} \psi_1(\mathbf{x}_1) \dots \psi_N(\mathbf{x}_N).$$

The spin-orbitals $\psi_k(\mathbf{x})$ are orthonormal.

(a) Show that the Slater determinant is normalised, by considering the inner product of two arbitrary terms occurring in the sum of the Slater determinant and then summing over all possible pairs of such terms.

(b) Show in the same way that the density of electrons with coordinates \mathbf{x} , given by

$$n(\mathbf{x}) = N \int dx_2 \dots dx_N |\Psi_{AS}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2,$$

can be written in terms of the ψ_k as:

$$n(\mathbf{x}) = \sum_k |\psi_k(\mathbf{x})|^2.$$

Suppose all spin-orbitals can be written as the product of a normalised orbital and a normalised one-particle spinor, what is then the spatial charge density of the electrons (i.e. regardless of the spin)?

Solution (a) Since all of the spin-orbitals $\psi_k(\mathbf{x})$ are orthonormal, the non-vanishing inner product of two arbitrary terms in the sum of the Slater determinant only occurs when their permutations are exactly same. Therefore,

$$\langle \Psi_{AS} | \Psi_{AS} \rangle = \int dx_1 dx_2 \dots dx_N |\Psi_{AS}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 = \frac{N!}{(\sqrt{N!})^2} = 1.$$

(b) There are $(N-1)!$ possibilities for the permutations from \mathbf{x}_2 to \mathbf{x}_N . Similarly, the density of electrons with coordinates \mathbf{x} is

$$n(\mathbf{x}) = N \int dx_2 \dots dx_N |\Psi_{AS}(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 = \frac{N \cdot (N-1)!}{(\sqrt{N!})^2} \sum_k |\psi_k(\mathbf{x})|^2 = \sum_k |\psi_k(\mathbf{x})|^2.$$

Since all spin-orbitals can be decomposed of normalised orbital and one-particle as the following:

$$\psi_k(\mathbf{x}) = \phi(\mathbf{r}) \chi(s).$$

The spatial charge density equals to

$$\rho(\mathbf{r}) = e \delta(\mathbf{r}) n(\mathbf{r}) = e \delta(\mathbf{r}) \sum_k |\psi_k(\mathbf{r})|^2.$$

6. In this problem we show that the large masses of the nuclei compared with those of the electrons lead to the Born-Oppenheimer approximation.

The wave function Ψ of a collection of electrons and nuclei depends on the position \mathbf{R}_n of the nuclei and \mathbf{r}_i of the electrons (we neglect the spin-degrees of freedom). For this function we make the following *Ansatz*:

$$\Psi(\mathbf{R}_n, \mathbf{r}_i) = \chi(\mathbf{R}_n)\Phi(\mathbf{r}_i)$$

with $\Phi(\mathbf{r}_i)$ an eigenstate with eigenvalue E_{el} of the N-electron 'Born-oppenheimer Hamiltonian', which in atomic units reads:

$$H_{BO} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 + \frac{1}{2} \sum_{i,j=1;i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{n=1}^K \sum_{i=1}^N \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|}.$$

It is clear that Φ and E_{el} depend on the nuclear positions \mathbf{R}_n , since the Born-Oppenheimer Hamiltonian does.

Show that substitution of this *Ansatz* into the full Hamiltonian leads to

$$\begin{aligned} & \Phi(\mathbf{r}_i) \left[\sum_{n=1}^K -\frac{1}{2M_n} \nabla_n^2 + E_{el} + \frac{1}{2} \sum_{n,n'=1;n \neq n'}^K \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}'_n|} \right] \chi(\mathbf{R}_n) \\ & - \chi(\mathbf{R}_n) \sum_{n=1}^K \frac{1}{2M_n} \nabla_n^2 \Phi(\mathbf{r}_i) - \sum_{n=1}^K \frac{1}{M_n} \nabla_n \chi(\mathbf{R}_n) \cdot \nabla_n \Phi(\mathbf{r}_i) = E \chi(\mathbf{R}_n) \Phi(\mathbf{r}_i), \end{aligned}$$

so that neglecting the last two terms on the left hand side of this equation, we arrive at a Schrödinger equation for the nuclei which contains the electronic degrees of freedom via the electronic energy E_{el} only:

$$\left[\sum_{n=1}^K -\frac{1}{2M_n} \nabla_n^2 + E_{el} + \frac{1}{2} \sum_{n,n'=1;n \neq n'}^K \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}'_n|} \right] \chi(\mathbf{R}_n) = E \chi(\mathbf{R}_n).$$

The fact that the term $(1/2M_n)\nabla_n^2\Phi(\mathbf{r}_i)$ can be neglected can be understood by realising that it is $1/M_n$ times the variation of the kinetic energy of the electrons with the positions of the nuclei. Of course, the core electrons have large kinetic energy, but they feel almost exclusively their own nucleus, hence their kinetic energy is insensitive to variations in the relative nuclear positions. The valence electrons have smaller kinetic energies, so the variation of this energy with nuclear positions will be small too. In a solid, deleting the term $(1/M_n)\nabla_n\chi(\mathbf{R}_n) \cdot \nabla_n\Phi(\mathbf{r}_i)$ means that electron-phonon couplings are neglected, so that some physical phenomena cannot be treated in calculations involving Born-Oppenheimer approach, although these effects can often be studied perturbatively.

Solution: The full Hamiltonian has the following form

$$\begin{aligned} H = & - \sum_{n=1}^K \frac{1}{2M_n} \nabla_n^2 - \sum_{i=1}^N \frac{1}{2m} \nabla_i^2 \\ & + \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{2} \sum_{i,j=1;i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{n=1}^K \sum_{i=1}^N \frac{Z_n}{|\mathbf{r}_i - \mathbf{R}_n|} + \frac{1}{2} \sum_{n,n'=1;n \neq n'}^K \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}'_n|} \right] \end{aligned}$$

The substitution of the given *Ansatz* into the full Hamiltonian leads to

$$H\Psi(\mathbf{R}_n, \mathbf{r}_i) = \left[\sum_{n=1}^K -\frac{1}{2M_n} \nabla_n^2 (\chi(\mathbf{R}_n) \Phi(\mathbf{r}_i)) \right] + \frac{e^2}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,n'=1; n \neq n'}^K \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}_{n'}|} (\chi(\mathbf{R}_n) \Phi(\mathbf{r}_i)) \\ + H_{BO}(\chi(\mathbf{R}_n) \Phi(\mathbf{r}_i)).$$

Consequently,

$$H\Psi(\mathbf{R}_n, \mathbf{r}_i) = \sum_{n=1}^K -\frac{1}{2M_n} [\Phi(\mathbf{r}_i) \nabla_n^2 \chi(\mathbf{R}_n) + \chi(\mathbf{R}_n) \nabla_n^2 \Phi(\mathbf{r}_i) + 2\nabla_n \chi(\mathbf{R}_n) \cdot \nabla_n \Phi(\mathbf{r}_i)] \\ + E_{el} \Phi(\mathbf{r}_i) \chi(\mathbf{R}_n) + \Phi(\mathbf{r}_i) \frac{e^2}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,n'=1; n \neq n'}^K \frac{Z_n Z_{n'}}{|\mathbf{R}_n - \mathbf{R}_{n'}|} \chi(\mathbf{R}_n) = E \Phi(\mathbf{r}_i) \chi(\mathbf{R}_n).$$

References

- [1] Jinbin Li. Note of Advanced Quantum Mechanics.
- [2] Adalberto Balzarotti, Michele Cini, Massimo Fanfoni. Atomi, Molecole e Solidi Esercizi Risolti, Seconda Edizione.
- [3] J.M.Thijssen. Computational Physics, Second edition.
- [4] Graham Woan. The Cambridge Handbook of Physics Formulas.