

Comments on the application of translational symmetry to accompany Steven Simon's *The Oxford Solid State Basics*

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Dedication: The present commentary was written because its author found Simon's book to be a very suitable textbook for an undergraduate course on basic solid state physics, and used it as such on two consecutive years. The choice of topics, the level of sophistication, the clarity of the exposition - are just right. However, being born into a culture that values intellectual dissent², the present author felt compelled to favour a more explicit application of symmetry in some of the derivations, which is what the present text humbly and respectfully attempts to offer.

Acknowledgements: These notes have greatly benefitted from the comments offered by Jiajie Gao, Qia Lin, Chang Liu, Xuqi Liu, Yiyang Yan, Bowen Yu and Wanting Zhang. Support of these students' endeavor by the management of GTIIT is gratefully acknowledged. The author is responsible for any remaining errors or obscurities. Comments by future readers will be most welcome.

Reading guide: You are hopefully familiar with most of section 1 (pages 1-10) that you are urged to review at the very beginning of the semester. This section aims to clarify the role of symmetry (*i. e.*, the existence of operators that commute with the Hamiltonian) in simplifying both variational calculations and the use of perturbation theory.

Sections 2 and 3 are associated with specific sections in Simon's textbook, but are (hopefully) familiar from your earlier studies. They illustrate the use of symmetry in simple atomic and molecular contexts, and are recommended for early review, before reaching the discussion of electronic wave functions in solids.

Sections 4 and 5 should be read in that order, along with chapter 11 in Simon's textbook. These sections deal with the role of the translational symmetry of a periodic lattice on its electronic states. They depend on section 1.2. In section 4 symmetry fully determines the electronic states, and in section 5 an additional step is required, involving the diagonalization of some matrix.

Sections 6 and 7 depend on section 1 but are independent of one another or of sections 4-5. Section 6, that depends strongly on section 1.3, deals with the role of symmetry in the treatment of a system of electrons interacting with a weak periodic potential. It should be read along with Simon's chapter 15. Sections 7.1-7.6 serve as a leisurely introduction to normal modes of a system of harmonically (*quadratically*) interacting masses and to the role (and limitations) of symmetry in their analysis. These sections are recommended to be read ahead of Simon's chapter 9. The remaining parts of section 7 should be read along with

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²Meant as a sign of respect to the person we argue with.

Simon's chapter 9.

To keep track of the apparent complexity of this section it will be useful to keep in mind that symmetry sometimes allows a complete solution of the normal mode problem, but more often leaves some further effort (another matrix diagonalization). Furthermore, the normal mode analysis can be carried out within Newtonian (classical) mechanics, quantizing at the end, or it can be carried out within quantum mechanics from the outset, yielding the same final description. Finally, two "pictures" are encountered, one (the "atomic displacement picture") yielding arrays of coherently oscillating displacements of the various masses from their equilibrium positions, and the other (the "normal coordinate picture") yielding a set of linear combinations of atomic displacements that allow a separation of the harmonic Hamiltonian into a sum of non-interacting terms.

Section 8 is offered as supplementary reading on the summer vacation that follows your successful completion of the Solid State course.

Reading advice: There are occasional questions and exercises throughout the text. They are meant to be answered as you read. When reading a text of the present type, you should develop the habit of reading slowly. Keep asking yourself "why?" while reading any statement. Insist on experiencing the satisfaction of having understood new ideas.

1. Review of quantum mechanical preliminaries

In the present section we review basic concepts and results that are needed in the following sections.

1.1 Some basics

Here we review properties of operators that are relevant to quantum mechanics. You may find that the notion of unitary operator is new, but please notice its connection with Hermitian operators.

We begin by recalling some results that you hopefully encountered in an earlier quantum mechanics (or quantum chemistry) course, but tried to forget as soon as the final examination was over.³

This text is meant for self-study, so it is intertwined with (hopefully) simple exercises that you are strongly urged to deal with when you encounter them.

Exercise: Please choose the correct answer: Why is it important to solve the exercises as we proceed?

1. Because the author of this text was too lazy to write the solutions for us.
2. Because the author wants us to suffer, like he did when he was an undergraduate.
3. Because this is the way to really be confident that we understand what we are reading.

³The author of these notes tries to compete with Simon's lovely sense of humor.

4. Because the author gets paid to turn us into obedient citizens.

Everything that we do here takes place within a **linear space of functions** of some set of variables (usually the spatial coordinates of a certain set of particles). By “linear space” we mean that if f and g belong to the space, then so does any linear combination $\alpha f + \beta g$, where α and β are two (real or complex) constants. f^* denotes the complex conjugate of f . The integral $\int f^* g dv$, taken over the whole range of the coordinates that f and g depend on, is referred to as the scalar product of the functions f and g . If, for all functions f in the linear space, the integral $\int f^* f dv$ is finite, then we say that our linear space of functions is a **Hilbert space**. We do not insist on mathematical subtleties (but we are happy to know that mathematicians are watching our heuristic steps to keep us away from trouble).

The fact that $\int f^* f dv < \infty$ implies that $\tilde{f} = \frac{f}{\sqrt{\int f^* f dv}}$ satisfies $\int \tilde{f}^* \tilde{f} dv = 1$. We say that \tilde{f} is **normalized**. Hence, $\tilde{f}^* \tilde{f} = |\tilde{f}|^2$ can be interpreted as a probability density. For example, for a single particle moving on a straight line with $-\infty \leq x \leq \infty$ the probability that the coordinate x obtains a value between x and $x + dx$ is $|f(x)|^2 dx$. If $\int f^* g dv = 0$ we say that f and g are **orthogonal**.

Having defined a linear space of functions, we define **operators**, that specify mappings (transformations) between functions in our space. If \hat{O} is such an operator, then the symbol $\hat{O}f$, that we read as \hat{O} acting on f , is a function within our linear space. We say that \hat{O} is a **linear operator** if $\hat{O}(\alpha f + \beta g) = \alpha \hat{O}f + \beta \hat{O}g$ for every pair of functions, f, g , in our linear space, where α and β are (again) any two constants.

Exercise: Please show that the derivative, $\frac{d}{dx}$, is a linear operator.

Is the second derivative, $\frac{d^2}{dx^2}$, a linear operator?

Please show that the square root, $\sqrt{\quad}$, is not a linear operator.

Is exponentiation, the operator that takes f into $\exp(f)$, a linear operator?

From now on, when we say “operator” we mean “linear operator”.

In many applications we encounter expressions of the form $\int f^*(\hat{O}g)dv$. The parentheses are usually omitted. We use them (once) to emphasize that $\hat{O}g$ is a function produced by the action of \hat{O} on g . If we can find an operator, that we denote by \hat{O}^\dagger , such that $\int (\hat{O}^\dagger f)^* g dv = \int f^*(\hat{O}g)dv$ for every pair of functions f and g in our Hilbert space, then we say that \hat{O}^\dagger is the **Hermitian conjugate** of \hat{O} .

In the special case $\hat{O}^\dagger = \hat{O}$ we say that \hat{O} is a **Hermitian operator**.

We say that two operators, \hat{A} and \hat{B} , are equal if the functions $\hat{A}f$ and $\hat{B}f$ are equal for all functions f in our linear space.

Exercise: Any function, $f(x)$, in the Hilbert space of functions of $-\infty < x < \infty$, satisfies $\int_{-\infty}^{\infty} f^*(x)f(x)dx < \infty$.

Please explain why such a function must vanish both for $x \rightarrow \infty$ and for $x \rightarrow -\infty$.

Please show that the operator \hat{x} , defined by $\hat{x}f(x) = xf(x)$, is Hermitian.
 Please show that the derivative operator (defined above) is not Hermitian.
 Please show that the operator $\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$ is Hermitian.

If a function ϕ satisfies $\hat{O}\phi = \lambda\phi$, where λ is a constant, we say that ϕ is an **eigenfunction** of the operator \hat{O} . The constant λ is referred to as the corresponding **eigenvalue**.

You are (hopefully) familiar with the following three properties of any Hermitian operator:

1. The eigenvalues of a Hermitian operator are real.
2. Two eigenfunctions that belong to distinct eigenvalues are orthogonal.⁴
3. The eigenfunctions constitute a complete set in the corresponding Hilbert space.

Exercise:

1. Using the Hermiticity of \hat{O} , we note that

$$\int f^* \hat{O} f dv = \int (\hat{O} f)^* f dv .$$

If $\hat{O}f = \lambda f$, please prove that the eigenvalue λ is real.

2. Furthermore, using

$$\int f^* \hat{O} g dv = \int (\hat{O} f)^* g dv ,$$

where f and g are eigenfunctions of \hat{O} with distinct eigenvalues $\lambda \neq \mu$, please prove that $\int f^* g dv = 0$.

The third property will be applied quite often, but its proof requires more advanced mathematics.

It may be useful to recall that a **complete set of functions** in a linear space allows any function in the corresponding space to be written as a (unique) linear combination of these functions. Each member of a complete set of functions is linearly independent of all the others (it cannot be written as a linear combination of all these other functions). If this is not true then we say that the set is overcomplete. It is convenient to assume that the complete set consists of orthonormal functions (each function is normalized and any two distinct functions are orthogonal).

Since it will be so important, we shall now glorify the second property of Hermitian operators, stated and proved above, repeating it as

Theorem I: Two eigenfunctions of a Hermitian operator that belong to distinct eigenvalues are orthogonal.

⁴A Lemma stated on the following page deals with the case of two or more (linearly independent) eigenfunctions of the Hermitian operator \hat{O} that belong to the same eigenvalue.

To proceed, we define the product of two (linear) operators, \hat{A} and \hat{O} , by the requirement that

$$(\hat{A}\hat{O})f = \hat{A}(\hat{O}f) \quad (1)$$

should hold for any function f in the Hilbert space in which \hat{A} and \hat{O} are defined. The right-hand side of equation (1) means that we first apply the operator \hat{O} on f , producing the function $\hat{O}f$, on which we apply the operator \hat{A} .

We are now ready to introduce a property that we need throughout the semester.

Theorem II: If two Hermitian operators, \hat{O} and \hat{A} , commute, *i. e.*,

$$\hat{O}\hat{A} = \hat{A}\hat{O},$$

then any two eigenfunctions of \hat{A} , f and g , that correspond to distinct eigenvalue $\lambda \neq \mu$ satisfy

$$\int f^* \hat{O}g dv = 0.$$

Exercise: Please prove theorem II, starting from the equality

$$\int (\hat{O}f)^*(\hat{A}g)dv = \int f^* \hat{O}(\hat{A}g)dv = \int f^* (\hat{O}\hat{A})g dv = \int f^* (\hat{A}\hat{O})g dv = \int (\hat{A}f)^* \hat{O}g dv.$$

It will be demonstrated below how the theorems stated above allow the search for the eigenfunctions (and the corresponding eigenvalues) of the operator \hat{O} to be simplified by first considering the eigenfunctions of an operator \hat{A} , that commutes with \hat{O} . Here, it is important to keep in mind the following property

Lemma: Any linear combination of two (or more) eigenfunctions of a linear operator \hat{A} with a common eigenvalue is an eigenfunction of \hat{A} with the same eigenvalue.

Exercise: Please prove this Lemma.

A concept that we did not use in Quantum Chemistry, that will be useful here, is the concept of **Unitary operator**. Before we define a unitary operator it will be necessary to define the **inverse of an operator**, \hat{A} , as the operator, that we denote by \hat{A}^{-1} , that satisfies the property $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{I}$, where \hat{I} is the **identity operator**, the operator that does nothing (just like adding zero to a number, or multiplying it by 1). If $\hat{A}\phi = \psi$ then $\phi = \hat{A}^{-1}\psi$. It follows that only operators which do not have zero as an eigenvalue (in other words, operators whose action on any function in the Hilbert space never produces zero) can have an inverse.

Exercise: Please be sure that you understand the reason for the restriction in the last sentence.

A **unitary operator** is an operator, \hat{U} , that satisfies the property $\hat{U}^\dagger = \hat{U}^{-1}$. In other words, the Hermitian conjugate of a unitary operator is equal to its inverse. This property

means that if the function ψ is normalized (i. e., $\langle\psi|\psi\rangle = 1$) then $\hat{U}\psi$ is normalized as well.

Exercise: Prove this property, starting from $\langle\hat{U}\psi|\hat{U}\psi\rangle$ and showing that it is equal to $\langle\psi|\psi\rangle$.

Exercise: Using the property you just proved, show that if ψ is an eigenfunction of the unitary operator \hat{U} with the eigenvalue λ , then $|\lambda|^2 = \lambda^*\lambda = 1$, which means that λ can be written in the form $\exp(i\zeta)$, where ζ is a real number. Obviously, the eigenvalues of a unitary operator are not restricted to be real.

Moreover, from the result you just proved it follows that if ψ is an eigenfunction of the unitary operator \hat{U} with the eigenvalue λ , then it is also an eigenvalue of \hat{U}^\dagger with the eigenvalue λ^* .

It is not difficult to prove that two eigenfunctions of a unitary operator, that belong to distinct eigenvalues, must be orthogonal. This property is very similar to Theorem I, stated above for Hermitian operators. If the unitary operator \hat{U} commutes with some operator \hat{A} , then the matrix element of \hat{A} between two eigenfunctions of \hat{U} with distinct eigenvalues vanishes. This is very similar to Theorem II, stated above.

To understand the resemblance between the properties of Hermitian and unitary operators it may be worthwhile to note that if \mathcal{O} is Hermitian then $\hat{U} = \exp(i\alpha\mathcal{O})$, where α is a real parameter, is unitary. This follows from the fact that the Hermitian conjugate of \hat{U} is $\exp(-i\alpha\mathcal{O})$, which is just \hat{U}^{-1} . If \mathcal{O} commutes with \mathcal{H} , so does \hat{U} . If ψ is an eigenfunction of \mathcal{O} with the (real) eigenvalue ζ then it is an eigenfunction of \hat{U} with the eigenvalue $\exp(i\alpha\zeta)$, and an eigenfunction of $\hat{U}^\dagger = \hat{U}^{-1}$ with the eigenvalue $\exp(-i\alpha\zeta)$.⁵

Exercise: Please prove all the claims made in the last paragraph.

Exercise: Please state carefully the analogues of Theorem I and Theorem II for a unitary operator.

Instead of first introducing Hermitian operators and then unitary operators, and realizing that they have similar properties, we could introduce **Normal Operators**, which are defined by the fact that they commute with their Hermitian conjugates.⁶ Hermitian operators are trivially normal (why?), and unitary operators are normal as well (recall that if \hat{U} is unitary then $\hat{U}^\dagger = \hat{U}^{-1}$). It is quite easy to generalize the proof of the basic properties of Hermitian operators and show

- If ψ is an eigenfunction of the normal operator \hat{A} with the eigenvalue λ , then ψ is also

⁵To understand this property we note that if $\hat{O}\phi = \lambda\phi$ then $\hat{O}^2\phi = \lambda^2\phi$ and $\hat{O}^k\phi = \lambda^k\phi$. Moreover, if $f(x)$ can be written as a power series $f(x) = \sum_{\ell=0}^{\infty} f_\ell x^\ell$ then

$$f(\hat{O})\phi = \sum_{\ell=0}^{\infty} f_\ell \hat{O}^\ell \phi = \sum_{\ell=0}^{\infty} f_\ell \lambda^\ell \phi = f(\lambda)\phi.$$

⁶I am only familiar with one introductory textbook on quantum chemistry, F. L. Pilar, Elementary Quantum Chemistry, Dover 2013, that introduces normal operators.

an eigenfunction of $\hat{\Lambda}^\dagger$, with the eigenvalue λ^* .

- Two eigenfunctions of a normal operator with distinct eigenvalues are orthogonal.
- If the normal operator $\hat{\Lambda}$ commutes with the operator \mathcal{A} and ϕ, ψ are two eigenfunctions of $\hat{\Lambda}$ with distinct eigenvalues, then $\langle \phi | \mathcal{A} | \psi \rangle = 0$.

In an introductory course it makes sense to restrict our attention to Hermitian operators, because they have real eigenvalues and, therefore, can be associated with (physical) observables - that we measure in the laboratory.

Although **normal operators** form a larger set, containing both Hermitian and unitary operators, even in elementary quantum mechanics we encountered operators that are not normal, namely the harmonic oscillator operators $\hat{a} = \frac{1}{\sqrt{2}}(\hat{p} - i\hat{x})$ and $\hat{a}^\dagger = \frac{1}{\sqrt{2}}(\hat{p} + i\hat{x})$ or the angular momentum operators $\hat{L}_+ = \hat{L}_x + i\hat{L}_y$ and $\hat{L}_- = \hat{L}_x - i\hat{L}_y = \hat{L}_+^\dagger$. These operators are not normal because \hat{a} and \hat{a}^\dagger do not commute (and, similarly, \hat{L}_- and \hat{L}_+ do not commute).

1.2 Symmetry and the variational principle

If the Hamiltonian commutes with some Hermitian or unitary operator, its eigenfunctions can be constructed in such a way that they are at the same time eigenfunctions of this additional operator. This can be used to simplify the construction of these eigenfunctions, as explained in the present section. Later on, we use this idea to deal with several problems related to the electronic structure and to the motions of the nuclei in solids.

We will apply the Theorems and the Lemma stated above to problems where we wish to determine the eigenfunctions and eigenvalues of a Hermitian operator \mathcal{H} (the Hamiltonian describing some physical system). The most common approach involves the application of the linear variational principle: We choose a set of functions $\phi_1, \phi_2, \dots, \phi_N$ and construct linear combinations of these functions in order to approximate the eigenfunctions of \mathcal{H} . Considering an arbitrary linear combination

$$\Psi = c_1\phi_1 + c_2\phi_2 + \dots + c_N\phi_N$$

we evaluate the expectation value of the Hamiltonian operator, defined by

$$\mathcal{E} = \frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

The variational principle tells us that $\mathcal{E} \geq E_g$, where E_g is the ground state energy (*i. e.*, lowest eigenvalue) of our Hamiltonian⁷.

Minimizing \mathcal{E} with respect to the N linear variables c_1, c_2, \dots, c_N , followed by some linear algebra, we find that we need to solve the matrix eigenvalue equation

$$\begin{pmatrix} H_{1,1} & H_{1,2} & \cdots & H_{1,N} \\ H_{2,1} & H_{2,2} & \cdots & H_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N,1} & H_{N,2} & \cdots & H_{N,N} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} = \mathcal{E} \begin{pmatrix} S_{1,1} & S_{1,2} & \cdots & S_{1,N} \\ S_{2,1} & S_{2,2} & \cdots & S_{2,N} \\ \vdots & \vdots & \ddots & \vdots \\ S_{N,1} & S_{N,2} & \cdots & S_{N,N} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}, \quad (2)$$

where

$$H_{i,j} = \int \phi_i^* \mathcal{H} \phi_j d\tau = \langle \phi_i | \mathcal{H} | \phi_j \rangle$$

and

$$S_{i,j} = \int \phi_i^* \phi_j d\tau = \langle \phi_i | \phi_j \rangle.$$

⁷The mathematician watching behind our back would tell us that we have to state that our Hamiltonian possesses such a “lowest eigenvalue”, or - as she would like to say - “is bounded from below”. This property holds for all the systems we will consider.

The integrations range over the whole space of the coordinates and $d\tau$ is the volume element. We obtain N eigenvalues⁸ $\mathcal{E}_1 \leq \mathcal{E}_2 \leq \dots \leq \mathcal{E}_N$, each of which is associated with an eigenvector

$$\begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix}.$$

This is, in principle, straightforward, but the matrix that needs to be diagonalized can be quite large.

Exercise: Please verify that you can derive equation (2) for the special cases $n = 1, 2$.

If there is a (unitary or Hermitian) operator, \hat{O} , that commutes with the Hamiltonian (such an operator is usually related to some symmetry property of the physical system considered), then we can gain considerable simplification if each one of the functions $\phi_1, \phi_2, \phi_3, \dots, \phi_N$ is an eigenfunction of \hat{O} . Quite often, the set of functions that we choose to use in our variational treatment of some Hamiltonian does not satisfy this property, but it does satisfy a “weaker” property: the action of the (Hermitian or unitary) operator \hat{O} on each one of these functions can be expressed as a linear combination of these functions only. If this property is satisfied we say that the N -dimensional linear space spanned by these functions is an **invariant subspace** under the action of \hat{O} .⁹ In such a case we can construct linear combinations of the N functions $\phi_1, \phi_2, \dots, \phi_N$, each one of which is an eigenfunction of the operator \hat{O} with some eigenvalue λ . We simply note that the invariance of the subspace defined above under the action of \hat{O} means that

$$\hat{O}\phi_i = \sum_{j=1}^N c_{i,j}\phi_j \quad ; \quad i = 1, 2, \dots, N,$$

⁸It can be shown that if $E_1 \leq E_2 \leq E_3 \leq \dots \leq E_N$ are the N lowest exact eigenvalues of the Hamiltonian considered, then $E_1 \leq \mathcal{E}_1, E_2 \leq \mathcal{E}_2, E_3 \leq \mathcal{E}_3, \dots, E_N \leq \mathcal{E}_N$.

⁹We note in passing that a finite-dimensional subspace of functions can be invariant under the action of several distinct operators. If such a subspace is invariant under two operators, \hat{O}_1 and \hat{O}_2 , then the following two properties hold:

1. This subspace is invariant under the action of the product of the two operators, $\hat{O}_1\hat{O}_2$, (as well as under the action of their product in the opposite order, $\hat{O}_2\hat{O}_1$).
2. This subspace is invariant under the action of the commutator of the two operators, $[\hat{O}_1, \hat{O}_2] = \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1$.

(please prove these claims). Repeated application of the first property generates, under some “technical” restrictions that we do not want to go into, a set of operators that form a **group**, and repeated application of the second generates a **Lie algebra**. You are familiar with the Lie algebra formed by the commutators of the three components, $\hat{L}_x, \hat{L}_y, \hat{L}_z$, of the angular momentum operator. These operators are related to rotations in space. The general theory of groups, Lie algebras, the connection between them, and their applications to quantum mechanics is a fascinating topic, that I strongly advise you to seek an opportunity to learn.

so the requirement that

$$\hat{O} \sum_{\ell=1}^N \alpha_{\ell} \phi_{\ell} = \lambda \sum_{\ell=1}^N \alpha_{\ell} \phi_{\ell}$$

yields the matrix eigenvalue problem

$$\sum_{\ell=1}^N \alpha_{\ell} c_{\ell,j} = \lambda \alpha_j.$$

Here, we seek the eigenvalues λ and the corresponding eigenvectors $(\alpha_1, \alpha_2, \dots, \alpha_N)$ of the matrix $\{c_{i,j} ; i = 1, 2, \dots, N, j = 1, 2, \dots, N\}$.

We shall assume, for simplicity, that the basis functions specified above have already been chosen to be eigenfunctions of \hat{O} .

To illustrate these ideas we consider the derivative operator, $\hat{D} \equiv \frac{d}{dx}$. Obviously, the pair of functions $\{\sin(\alpha x), \cos(\alpha x)\}$ span an invariant subspace with respect to $\frac{d}{dx}$.

Exercise:

1. Please verify this statement.
2. Please verify that the set of functions $\{\sin(x), \cos(2x)\}$ does not span an invariant subspace.
3. Please form linear combinations of $\sin(\alpha x)$ and $\cos(\alpha x)$ that are eigenfunctions of $\frac{d}{dx}$. What are the corresponding eigenvalues?

We now assume that some N_1 of the N basis functions we consider, $\phi_1, \phi_2, \dots, \phi_{N_1}$, are eigenfunctions of \hat{O} with a common eigenvalue λ_1 , (we say that they are degenerate with respect to \hat{O}), while the eigenvalues with respect to \hat{O} of all the remaining basis functions, $\phi_{N_1+1}, \phi_{N_1+2}, \dots, \phi_N$, are not equal to λ_1 (there may be additional degeneracies among those other basis functions). From the results established above it follows that whenever $1 \leq i \leq N_1$ and $N_1 + 1 \leq j \leq N$, the matrix elements $H_{i,j}$ and $S_{i,j}$ both vanish. So do $H_{j,i} = H_{i,j}^*$ and $S_{j,i} = S_{i,j}^*$. As a consequence, the $N \times N$ matrix is “block diagonal”, *i. e.*, it is of the form

$$\begin{pmatrix} H_{1,1} & H_{1,2} & \cdots & H_{1,N_1} & 0 & 0 & \cdots & 0 \\ H_{2,1} & H_{2,2} & \cdots & H_{2,N_1} & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ H_{N_1,1} & H_{N_1,2} & \cdots & H_{N_1,N_1} & 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 & H_{N_1+1,N_1+1} & H_{N_1+1,N_1+2} & \cdots & H_{N_1+1,N} \\ 0 & 0 & \cdots & 0 & H_{N_1+2,N_1+1} & H_{N_1+2,N_1+2} & \cdots & H_{N_1+2,N} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 0 & H_{N,N_1+1} & H_{N,N_1+2} & \cdots & H_{N,N} \end{pmatrix}.$$

The same is true for the matrix of overlap integrals, $S_{i,j}$. The corresponding eigenvalue

equation splits into an $N_1 \times N_1$ matrix equation,

$$\begin{vmatrix} H_{1,1} - ES_{1,1} & H_{1,2} - ES_{1,2} & \cdots & H_{1,N_1} - ES_{1,N_1} \\ H_{2,1} - ES_{2,1} & H_{2,2} - ES_{2,2} & \cdots & H_{2,N_1} - ES_{2,N_1} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N_1,1} - ES_{N_1,1} & H_{N_1,2} - ES_{N_1,2} & \cdots & H_{N_1,N_1} - ES_{N_1,N_1} \end{vmatrix} = 0,$$

and a totally decoupled $(N - N_1) \times (N - N_1)$ matrix equation for the eigenfunctions of \hat{O} with different eigenvalues (we sometimes say “eigenfunctions with different symmetries”).

In the most favorable applications that we consider below, the eigenvalues of the “symmetry” operator \hat{O} are sufficient to generate a new basis of the invariant subspace spanned by $\phi_1, \phi_2, \dots, \phi_N$, such that each member of the new basis is specified by a unique eigenvalue. Constructing the $N \times N$ matrix of the Hamiltonian in terms of this “symmetry-adapted” basis we note that it is diagonal, hence

$$E_i = \frac{\langle \phi_i | \mathcal{H} | \phi_i \rangle}{\langle \phi_i | \phi_i \rangle}, \quad i = 1, 2, \dots, N.$$

In less favorable cases we find that the N -dimensional invariant subspace contains several linearly independent eigenfunctions of the symmetry-operator \hat{O} with a common eigenvalue. In such cases we need to diagonalize matrices whose sizes are equal to the number of degenerate basis functions for any particular eigenvalue of \hat{O} .

1.3 Symmetry and perturbation theory

Symmetry properties of the Hamiltonian (the existence of a Hermitian or a unitary operator that commutes with the Hamiltonian) simplify the application of perturbation theory, in particular (but not only) when the unperturbed Hamiltonian possesses degenerate eigenfunctions. This is explained here and used in Section 6, where we investigate the effect of a potential which is periodic in space on electrons that are otherwise free.

You are certainly familiar with perturbation theory from your earlier studies. The starting point is a Hamiltonian that can be written in the form

$$\mathcal{H} = \mathcal{H}_0 + \lambda V,$$

where \mathcal{H}_0 is simple enough, so that we know how to obtain all its eigenfunctions and eigenvalues

$$\mathcal{H}_0 \phi_n^{(0)} = E_n^{(0)} \phi_n^{(0)},$$

and V is “small” (in some sense that we do not try to define rigorously). λ is a parameter that is introduced to keep track of the order of the various terms in the expressions for the eigenvalues and eigenfunctions of the Hamiltonian. It is usually set equal to 1 at the end of

the derivation.

We recall that if the eigenvalue $E_n^{(0)}$ of \mathcal{H}_0 corresponds to a unique eigenfunction $\phi_n^{(0)}$ (we say that it is non-degenerate) then we can approximate the corresponding eigenvalue of \mathcal{H} by

$$E_n = E_n^{(0)} + \lambda \langle \phi_n^{(0)} | V | \phi_n^{(0)} \rangle + \lambda^2 \sum_{n' \neq n} \frac{|\langle \phi_n^{(0)} | V | \phi_{n'}^{(0)} \rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}} + \dots$$

If the eigenvalue $E_n^{(0)}$ corresponds to two (or more) distinct eigenfunctions $\phi_{n,1}^{(0)}, \phi_{n,2}^{(0)}, \dots$, (that we assume to be orthonormal) then the second order term involving $|\langle \phi_{n,1}^{(0)} | V | \phi_{n,2}^{(0)} \rangle|^2$ has a vanishing denominator. If $\langle \phi_{n,1}^{(0)} | V | \phi_{n,2}^{(0)} \rangle$ vanishes (a case we will discuss below) then we can proceed as above, but otherwise we need to apply the formalism of degenerate first order perturbation theory, that involves the diagonalization of the matrix

$$\begin{pmatrix} \langle \phi_{n,1}^{(0)} | V | \phi_{n,1}^{(0)} \rangle & \langle \phi_{n,1}^{(0)} | V | \phi_{n,2}^{(0)} \rangle & \dots \\ \langle \phi_{n,2}^{(0)} | V | \phi_{n,1}^{(0)} \rangle & \langle \phi_{n,2}^{(0)} | V | \phi_{n,2}^{(0)} \rangle & \dots \\ \dots & \dots & \dots \end{pmatrix},$$

within the (usually finite dimensional) subspace of the degenerate eigenfunctions $\phi_{n,1}^{(0)}, \phi_{n,2}^{(0)}, \dots$ of \mathcal{H}_0 that correspond to the eigenvalue $E_n^{(0)}$.

An important special case (that is not always mentioned in introductory courses) involves the case in which both \mathcal{H}_0 and V commute with some operator \hat{O} . From the fact that \mathcal{H}_0 commutes with \hat{O} it follows that $\hat{O}\phi_{n,i}^{(0)}$ is an eigenfunction of \hat{H}_0 with the same eigenvalue as $\phi_{n,i}^{(0)}$.

Exercise: Please be sure that you know how to verify this claim.

It follows that all $\hat{O}\phi_{n,i}^{(0)}$; $i = 1, 2, \dots$ belong in the subspace spanned by the degenerate zero-order functions $\phi_{n,i}^{(0)}$; $i = 1, 2, \dots$ and can be written as linear combinations of the latter. In this way we generate a matrix whose diagonalization produces functions that are at the same time eigenfunctions of \mathcal{H}_0 (all with the same eigenvalue $E_n^{(0)}$) and of \hat{O} . We will denote these functions by $\tilde{\phi}_{n,i}^{(0)}$; $i = 1, 2, \dots$. If each of these functions corresponds to a distinct eigenvalue of \hat{O} then it follows from the fact that \hat{O} commutes with V that the off-diagonal matrix elements $\langle \phi_{n,i}^{(0)} | V | \phi_{n,j}^{(0)} \rangle$; $i \neq j$ all vanish. If this holds then the formalism of non-degenerate perturbation theory can be applied in the basis $\tilde{\phi}_{n,i}^{(0)}$, despite the degeneracy.

2. Simon, Chapter 19.2.1: Singlet and triplet states of the excited helium atom

Whenever you encounter a section heading that contains a reference to a specific part of Simon's textbook, what you find here should be read together with that section. No effort is made to make the present text self-contained, let alone a substitute for Simon's corresponding section. It is strictly an addendum, which the present author hopes you will find helpful.

The present section is a simple illustration of the role of symmetry (in this case, the symmetry of the two-electron atomic Hamiltonian with respect to transposition of the two electrons) in a variational computation. The results form an introduction to the electronic origin of magnetic interactions in (some) solids.

This section and the next one are reviews of things you learnt in Quantum Chemistry. You are urged to read them now because they illustrate in a familiar context some ideas that we will use soon afterwards. It may be a good idea to read these sections again when you reach the corresponding chapters in Simon's textbook.

The Hamiltonian of the helium-like atom is

$$\mathcal{H} = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}, \quad (3)$$

where r_1 and r_2 are the distances of the two electrons from the nucleus, and r_{12} is the distance between the two electrons. Obviously, this Hamiltonian is symmetric with respect to a transposition of the indices ("names") of the two electrons. We introduce the operator \hat{P}_{12} , which satisfies the property

$$\hat{P}_{12}\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1),$$

for any function of \vec{r}_1 and \vec{r}_2 . Obviously, this operator commutes with the Hamiltonian of the helium atom. It follows that we can construct the eigenfunctions of the Hamiltonian such that each one of them is an eigenfunction of \hat{P}_{12} as well. Specifically, if we try to write an approximate wave function for the first excited state as a product of a function of one electron in the 1s orbital and another electron in the 2s orbital, it is convenient to start from the symmetric and the antisymmetric combinations

$$\psi_+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left(\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) + \phi_{2s}(\vec{r}_1)\phi_{1s}(\vec{r}_2) \right)$$

and

$$\psi_-(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left(\phi_{1s}(\vec{r}_1)\phi_{2s}(\vec{r}_2) - \phi_{2s}(\vec{r}_1)\phi_{1s}(\vec{r}_2) \right),$$

which are eigenfunctions of \hat{P}_{12} with the eigenvalues 1 and -1 , respectively. Here, we assume that $\langle \phi_{1s} | \phi_{1s} \rangle = \langle \phi_{2s} | \phi_{2s} \rangle = 1$, and $\langle \phi_{1s} | \phi_{2s} \rangle = 0$. It follows from Theorem I that

$$\langle \psi_+(\vec{r}_1, \vec{r}_2) | \psi_-(\vec{r}_1, \vec{r}_2) \rangle = 0$$

and from Theorem II that

$$\langle \psi_+(\vec{r}_1, \vec{r}_2) | \mathcal{H} | \psi_-(\vec{r}_1, \vec{r}_2) \rangle = 0.$$

Since the Pauli principle tells us that the total wave function must be antisymmetric with respect to permutation of the two electrons, we must multiply $\psi_+(\vec{r}_1, \vec{r}_2)$ by an antisymmetric spin function, $\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$, to obtain the two-electron wave function

$$\Psi(1s2s, {}^1S) = \frac{1}{2} \left(1s(1)2s(2) + 2s(1)1s(2) \right) \left(\alpha(1)\beta(2) - \beta(1)\alpha(2) \right),$$

which is referred to as a singlet state.

Similarly, we must multiply $\psi_-(\vec{r}_1, \vec{r}_2)$ by one of the three symmetric spin functions, $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, or $\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$, to obtain the triplet of wave functions

$$\begin{aligned} \Psi(1s2s, {}^3S, M_s = 1) &= \frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 2s(1)1s(2) \right) \alpha(1)\alpha(2) \\ \Psi(1s2s, {}^3S, M_s = 0) &= \frac{1}{2} \left(1s(1)2s(2) - 2s(1)1s(2) \right) \left(\alpha(1)\beta(2) + \beta(1)\alpha(2) \right) \\ \Psi(1s2s, {}^3S, M_s = -1) &= \frac{1}{\sqrt{2}} \left(1s(1)2s(2) - 2s(1)1s(2) \right) \beta(1)\beta(2), \end{aligned}$$

where M_s is the z -component of the total spin. We do not need to specify this quantum number for the singlet state, where the only possible value is $M_s = 0$. The Hamiltonian, equation (3), does not depend on the spins of the electrons. Therefore, its expectation values with respect to these three wave functions, that correspond to the same (antisymmetric) function of the coordinates, are the same,

$$\langle \psi_-(\vec{r}_1, \vec{r}_2) | \mathcal{H} | \psi_-(\vec{r}_1, \vec{r}_2) \rangle = \langle \phi_{1s} | \hat{h}_1 | \phi_{1s} \rangle + \langle \phi_{2s} | \hat{h}_2 | \phi_{2s} \rangle + J - K,$$

where $\hat{h}_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i}$; $i = 1, 2$, and

$$\begin{aligned} J &= \int \int \phi_{1s}^2(r_1) \frac{1}{r_{12}} \phi_{2s}^2(r_2) dv_1 dv_2, \\ K &= \int \int \phi_{1s}(r_1) \phi_{2s}(r_1) \frac{1}{r_{12}} \phi_{1s}(r_2) \phi_{2s}(r_2) dv_1 dv_2. \end{aligned}$$

Similarly, the symmetric function of the coordinates yields

$$\langle \psi_+(\vec{r}_1, \vec{r}_2) | \mathcal{H} | \psi_+(\vec{r}_1, \vec{r}_2) \rangle = \langle \phi_{1s} | \hat{h}_1 | \phi_{1s} \rangle + \langle \phi_{2s} | \hat{h}_2 | \phi_{2s} \rangle + J + K,$$

suggesting that its energy is higher, by $2K$, than that of the three wave functions with an antisymmetric space factor (K can be shown to be positive). We emphasize that this difference in energies is due to the electrostatic interaction between the electrons, not to their

spins, a conclusion that also applies to ferromagnetic solids, that you will learn about later. ¹⁰

3. Simon, Chapter 6.2.2: The LCAO approximation for the molecular hydrogen ion, H_2^+

This section illustrates the use of spatial symmetry (reflection in a plane) to simplify the variational treatment of a simple diatomic molecule. The same basic ideas will be used in Section 4 to investigate electrons in a one-dimensional periodic lattice.

Let the two protons reside on the z axis, at the points A , specified by the coordinates $(0, 0, -\frac{R}{2})$, and B , specified by $(0, 0, \frac{R}{2})$. We start by choosing the set of functions

$$1s_A, 1s_B, 2s_A, 2s_B, 2p_{x,A}, 2p_{x,B}, 2p_{y,A}, 2p_{y,B}, 2p_{z,A}, 2p_{z,B}, \dots,$$

where $1s_A$ denotes an s orbital centered at A , etc., as the set to be used for the variational computations, a basis-set choice that gives rise to the LCAO description of the molecular orbitals. ¹¹ If we take some care, this set of functions will span the whole Hilbert space (in fact, it will be overcomplete), but these are theoretical concerns that we can ignore since we are going to truncate this set of functions into a fairly small subset.

The Hamiltonian that describes the motion of the electron subject to the Coulomb attraction by the two stationary nuclei at A and B is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}.$$

The distance between the electron and nucleus A is denoted by r_A . If the position of the electron is specified by (x, y, z) then $r_A = \sqrt{x^2 + y^2 + (z + \frac{R}{2})^2}$. Similarly, $r_B = \sqrt{x^2 + y^2 + (z - \frac{R}{2})^2}$. The Laplacian operator depends on the electron's coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

¹⁰Although the computation we carried out above suggests that the difference in energy between the triplet of wave functions with antisymmetric space factor and the single function ("singlet") with a symmetric space factor is due to the difference in the expectation value of $\frac{1}{r_{12}}$, this cannot be quite true because of another property of atoms that you learnt about in Quantum Chemistry, the virial theorem. Recall that the virial theorem tells us that the kinetic energy of an atom (the expectation value of the sum of the Laplacians of all the electrons in the atom) must be equal to minus the total energy. Hence, the kinetic energy must be higher in the triplet than in the singlet. This can only happen if we allow the one-electron wave functions ϕ_{1s} and ϕ_{2s} to obtain somewhat different shapes in these two states. Doing this we find that the triplet state of the He atom is indeed lower in energy than the singlet (in agreement with the spectroscopists' observation, known as Hund's rule), but this is due to the fact that the ϕ_{2s} function shrinks (to increase the expectation value of the Laplacian - the kinetic energy), thereby increasing the attraction to the nucleus as well. Very surprisingly, the expectation value of $\frac{1}{r_{12}}$ is higher in the triplet, but discussing this in detail will take us too far away.

¹¹The abbreviation LCAO stands for Linear Combination of Atomic Orbitals

This Hamiltonian has several symmetry properties:

- It is cylindrically symmetric, relative to the molecular (z) axis¹². This can be formulated by the statement that the Hamiltonian commutes with the operator $\hat{R}_z = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$, which is essentially the z component of the (orbital) angular momentum ($\hat{L}_z = \hbar \hat{R}_z$). Transforming to cylindrical coordinates $x = \rho \cos(\phi)$; $y = \rho \sin(\phi)$ it follows that $\hat{R}_z = -i \frac{\partial}{\partial \phi}$. The eigenfunctions of this operator are $\exp(im\phi)$ where m has to be an integer to satisfy the physically plausible condition $f(\phi + 2\pi) = f(\phi)$. The notation $\sigma, \pi, \delta, \dots$ is used for eigenfunctions that correspond to the quantum number $m = 0, \pm 1, \pm 2, \dots$, respectively. You may have encountered the linear combinations $s_A \pm s_B$, $p_{x,A} \pm p_{x,B}$, (and $p_{y,A} \pm p_{y,B}$), $d_{xy,A} \pm d_{xy,B}$ (and $d_{x^2-y^2,A} \pm d_{x^2-y^2,B}$), that are eigenfunctions of \hat{R}_z with the eigenvalues $0, \pm 1, \pm 2, \dots$. They are referred to as σ orbitals, π orbitals, δ orbitals, \dots , respectively.
- The Hamiltonian of the electron in H_2^+ commutes with the operation of **reflection** through the plane (x, y) . This operation is usually denoted by $\hat{\sigma}_{xy}$. It interchanges the two nuclei, A and B. Functions which are antisymmetric (“odd”) under this operation, for example z or $\sin(z)$, are denoted with an asterisk (*). The linear combination $1s_A + 1s_B$ is cylindrically symmetric with respect to \hat{R}_z , and is symmetric (even) with respect to $\hat{\sigma}_{xy}$. It is denoted by the symbol σ , whereas $1s_A - 1s_B$, which is antisymmetric under the reflection operation, is denoted by σ^* . Obviously, a function which is odd under $\hat{\sigma}_{xy}$ vanishes on the xy -plane (we say that it has a planar node), a property which has implications with respect to the binding properties of such a function.
- Another symmetry operation that is commonly used is the **inversion** operation, \hat{i} , which takes the point (x, y, z) into $(-x, -y, -z)$. This can be described as drawing a straight line from the first point to the origin, and continuing it an equal distance on the other side. This operation, like the reflection introduced above, interchanges the nuclei, but for points in space which are not on the z axis these two operations are distinct. Functions, like $1s_A + 1s_B$, that are even under inversion, are denoted by the index g, *e. g.*, σ_g , and functions that are odd under inversion, such as $1s_A - 1s_B$, are denoted by the index u, such as σ_u^* .

Comments:

1. The exponential operator $\exp(i\alpha \hat{R}_z) = \exp\left(\alpha \frac{\partial}{\partial \phi}\right)$ can be defined by means of the Taylor series $\exp(x) = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$. It is not too difficult to show that

$$\exp\left(\alpha \frac{\partial}{\partial \phi}\right) f(\phi) = f(\phi + \alpha),$$

i. e., this operation acts as a rotation by the angle α around the z axis¹³ This is why

¹²What this means is that if we rotate the x and y axes in the plane which is perpendicular to the molecular axis (z), the form of the Hamiltonian is not changed.

¹³One way to prove this identity is to use the formal Taylor expansion

$$\exp\left(\alpha \frac{\partial}{\partial \phi}\right) = \sum_{\ell=0}^{\infty} \frac{\alpha^\ell}{\ell!} \frac{\partial^\ell}{\partial \phi^\ell}.$$

\hat{R}_z is often referred to as the generator of rotations around the z axis. The three angular momentum operators, $\hat{L}_x, \hat{L}_y, \hat{L}_z$, together generate any rotation through any axis that goes through the origin.

2. If an operator satisfies the identity $\hat{O}^k = \hat{I}$, where \hat{I} is the identity operator, then it is easy to show (whenever I say “it is easy to show”, please treat it as a suggestion to do it) that any eigenvalue of \hat{O} satisfies $\lambda^k = 1$, or $\lambda = \exp(i\frac{2\pi}{k}\ell)$, where $\ell = 0, 1, 2, \dots, k-1$. Specifically, for operators like $\hat{\sigma}_{xy}$ or \hat{i} , for which $k = 2$, the only eigenvalues are ± 1 .

3. A more complete discussion of the symmetry classification of molecular orbitals can be found in many textbooks on quantum chemistry or molecular spectroscopy.

4. Simon, Chapter 11: Translational symmetry and the tight-binding chain

Here we consider a system in which the (translational) symmetry of the Hamiltonian allows the eigenfunctions (more precisely, their variational approximation) to be completely determined.

Consider N identical atoms, equally placed on a circle, with a single orbital, ϕ_j , $j = 1, 2, \dots, N$, on each atom.

Let \hat{T} be a translation operator, such that

$$\begin{aligned}\hat{T}\phi_j &= \phi_{j+1} \quad \text{where } j = 1, 2, \dots, N-1, \\ \hat{T}\phi_N &= \phi_{N+1} = \phi_1. \quad \text{This is the periodic boundary condition.}\end{aligned}$$

We now consider linear combinations of these atomic orbitals (LCAO), $\Psi_\ell = \frac{1}{\sqrt{N}} \sum_{j=1}^N c_j \phi_j$, that we propose to use as variational approximations of the electronic wave functions. The overall coefficient $\frac{1}{\sqrt{N}}$ is inserted for convenience, but could be swallowed by the individual coefficients c_1, c_2, \dots, c_N . From the definition of the translation operator it follows that $\hat{T}^N \Psi_\ell = \Psi_\ell$ or $\hat{T}^N = 1$.

Let Ψ_ℓ be an eigenfunction of \hat{T} , *i. e.*,

$$\begin{aligned}\hat{T} \sum_{j=1}^N c_j \phi_j &= \lambda \sum_{j=1}^N c_j \phi_j, \\ &\text{and, on the other hand,} \\ &= \sum_{j=1}^N c_j \hat{T} \phi_j = \sum_{j=1}^N c_j \phi_{j+1} = \sum_{j=1}^N c_{j-1} \phi_j.\end{aligned}$$

Application of the right hand side of this operator identity on $f(\phi)$ yields the Taylor series expansion of $f(\phi + \alpha)$. An alternative derivation can be based on the fact that the identity is easily verified for any function of the form $\exp(im\phi)$ (where m is an integer), which is an eigenfunction of $\frac{\partial}{\partial \phi}$. Since any function $f(\phi)$ that satisfies $f(\phi + 2\pi) = f(\phi)$ can be written as a linear combination of these eigenfunctions (*i. e.*, as a Fourier series), the identity holds for $f(\phi)$ as well.

Here, $c_0 = c_N$. [**Question:** why was it OK to ignore the coefficient $\frac{1}{\sqrt{N}}$?]
It follows that $c_j = \frac{1}{\lambda} c_{j-1}$. Furthermore, $\lambda^N = 1$ so

$$\lambda = \exp\left(i\frac{2\pi}{N}\ell\right) \quad \text{where } \ell = 1, 2, \dots, N.$$

Hence,

$$c_j = \frac{1}{\lambda^j} c_0 = c_0 \exp\left(-i\frac{2\pi}{N}\ell j\right).$$

Finally, $\Psi_\ell = \frac{1}{\sqrt{N}} \sum_{j=1}^N \lambda^{-j} \phi_j$ (the overall factor c_0 was suppressed). For the sake of clarity we emphasize that Ψ_ℓ is a one-electron wave function, consisting of a linear combination of orbitals that are centered on the various atoms on the lattice, but all referring to the same electron. It is a generalization of the molecular orbital $\psi_{1s}(r_A) + \psi_{1s}(r_B)$ that we introduced in our discussion of the H_2^+ molecular ion. Specifying the origin at the lattice site 0 (or, by the periodic boundary condition, N) we denote the position of our electron by x . Because of the periodic boundary conditions x satisfies $0 \leq x \leq Na$. The position of the j 'th lattice site relative to the origin specified above is aj , where a is the distance between neighboring atoms (the lattice constant). The distance between the electron and the lattice point j is $x_j = x - ja$. Defining $L = Na$ we obtain

$$\begin{aligned} \Psi_\ell &= \frac{1}{\sqrt{N}} \sum_{j=1}^N \exp\left(-i\frac{2\pi}{L}alj\right) \phi_j \\ &= \frac{1}{\sqrt{N}} \sum_{j=1}^N \exp\left(-i\frac{2\pi}{L}\ell(x - x_j)\right) \phi_j \\ &= \frac{1}{\sqrt{N}} \exp\left(-i\frac{2\pi}{L}\ell x\right) \sum_{j=1}^N \exp\left(i\frac{2\pi}{L}\ell x_j\right) \phi_j. \end{aligned}$$

The factor $\frac{1}{\sqrt{N}} \sum_{j=1}^N \exp\left(i\frac{2\pi}{L}\ell x_j\right) \phi_j$ is periodic in the periodicity of the lattice. [Please verify this claim]. The factor $\exp\left(-i\frac{2\pi}{L}\ell x\right)$ is an eigenfunction of \hat{T} with the eigenvalue $\lambda = \exp\left(-i\frac{2\pi}{L}\ell a\right)$. [Please verify this claim as well]. These two facts are a special case of Bloch's theorem.

Let

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{j=1}^N v_j. \quad (4)$$

This Hamiltonian describes a single electron under the action of the N atomic potentials.¹⁴ Obviously, \mathcal{H} commutes with \hat{T} , so any two eigenfunctions of \hat{T} , with distinct eigenvalues,

¹⁴The N -electron Hamiltonian is a sum of N terms of the form (4), plus a term of the form $\sum_{i<j}^N \frac{1}{r_{ij}}$, that represents the interelectronic repulsion. The N -electron Hamiltonian commutes with the product of the N translation operators referring to the various electrons, which translates the coordinate of each one of them by a (keeping the interelectronic distances unchanged).

satisfy¹⁵

$$\langle \Psi_\lambda | \Psi_{\lambda'} \rangle = \delta_{\lambda, \lambda'} \langle \Psi_\lambda | \Psi_\lambda \rangle$$

and

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_{\lambda'} \rangle = \delta_{\lambda, \lambda'} \langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle,$$

$$\text{where } \delta_{\lambda, \lambda'} = \begin{cases} 1 & \text{if } \lambda = \lambda' \\ 0 & \text{if } \lambda \neq \lambda' \end{cases}.$$

We now evaluate

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle = \frac{1}{N} \sum_{j=1}^N \sum_{j'=1}^N \lambda^{j-j'} \langle \phi_j | \mathcal{H} | \phi_{j'} \rangle.$$

From the periodic boundary conditions it follows that the integral $\langle \phi_j | \mathcal{H} | \phi_{j'} \rangle$ depends only on the distance between the two lattice points j and j' , so we can write it in the form $\langle \phi_{j-j'} | \mathcal{H} | \phi_0 \rangle$. Hence,

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle = \frac{1}{N} \sum_{j=1}^N \sum_{j'=1}^N \lambda^{j-j'} \langle \phi_{j-j'} | \mathcal{H} | \phi_0 \rangle.$$

Replacing the inner sum (over j') by a sum over $n = j - j'$ and keeping in mind the periodic boundary conditions

$$\begin{aligned} \lambda^{n+N} &= \lambda^n && \text{because } \lambda^N = 1 \\ \langle \phi_n | \mathcal{H} | \phi_0 \rangle &= \langle \phi_{n+N} | \mathcal{H} | \phi_0 \rangle && \text{because } \phi_{n+N} = \phi_n \end{aligned}$$

we conclude that

$$\begin{aligned} \langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle &= \frac{1}{N} \sum_{j=1}^N \sum_{n=1}^N \lambda^n \langle \phi_n | \mathcal{H} | \phi_0 \rangle \\ &= \sum_{n=1}^N \lambda^n \langle \phi_n | \mathcal{H} | \phi_0 \rangle \end{aligned} \quad (5)$$

because in inner sum (over n) on the first line does not depend on j so the outer sum can be replaced by multiplication by the number of equal terms, N . Furthermore, assuming that the basis orbitals ϕ_j are real, it follows that

$$\langle \phi_j | \mathcal{H} | \phi_{j+n} \rangle = \langle \phi_j | \mathcal{H} | \phi_{j-n} \rangle.$$

Because of the periodic boundary conditions the atoms on the lattice behave as if they were on a circle of length N , so the distance between any two lattice sites cannot be larger than $\frac{N}{2}$. The term that corresponds to $n = N$ in equation (5) yields

$$\lambda^N \langle \phi_N | \mathcal{H} | \phi_0 \rangle = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle.$$

¹⁵The notation Ψ_λ is just a different notation for Ψ_ℓ , noting that $\lambda = \exp(-i\frac{2\pi}{L}a\ell)$.

Similarly, the terms that correspond to $n = 1$ and $n = N - 1$ yield, together

$$\lambda^1 \langle \phi_1 | \mathcal{H} | \phi_0 \rangle + \lambda^{N-1} \langle \phi_{N-1} | \mathcal{H} | \phi_0 \rangle = (\lambda + \lambda^{-1}) \langle \phi_1 | \mathcal{H} | \phi_0 \rangle,$$

etc. For even N it follows that

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle + \sum_{n=1}^{\frac{N}{2}-1} \left(\lambda^n \langle \phi_0 | \mathcal{H} | \phi_n \rangle + \lambda^{-n} \langle \phi_0 | \mathcal{H} | \phi_{N-n} \rangle \right) + \lambda^{\frac{N}{2}} \langle \phi_0 | \mathcal{H} | \phi_{\frac{N}{2}} \rangle,$$

and for odd N ,

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle + \sum_{n=1}^{\frac{N-1}{2}} \left(\lambda^n \langle \phi_0 | \mathcal{H} | \phi_n \rangle + \lambda^{-n} \langle \phi_0 | \mathcal{H} | \phi_{N-n} \rangle \right).$$

Assuming that the basis orbitals ϕ_j are real we note that the distance between ϕ_0 and ϕ_n is the same as the distance between ϕ_0 and ϕ_{N-n} (since $\phi_0 \equiv \phi_N$). Furthermore, we note that $\lambda^n + \lambda^{-n} = 2 \cos\left(n \frac{2\pi}{N} \ell\right)$ and $\lambda^{\frac{N}{2}} = \exp(-i\pi\ell) = \cos(\pi\ell) = (-1)^\ell$. Hence, for even N we obtain

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle = \langle \phi_0 | \mathcal{H} | \phi_0 \rangle + \sum_{n=1}^{\frac{N}{2}-1} 2 \cos\left(n \frac{2\pi}{N} \ell\right) \langle \phi_0 | \mathcal{H} | \phi_n \rangle + (-1)^\ell \langle \phi_0 | \mathcal{H} | \phi_{\frac{N}{2}} \rangle,$$

a slightly modified result holding for odd N . In order to evaluate the denominator in the variational expression for the energy we repeat the argument presented above, replacing the Hamiltonian, \mathcal{H} , by the identity operation. We obtain

$$\langle \Psi_\lambda | \Psi_\lambda \rangle = \langle \phi_0 | \phi_0 \rangle + \sum_{n=1}^{\frac{N}{2}-1} 2 \cos\left(n \frac{2\pi}{N} \ell\right) \langle \phi_0 | \phi_n \rangle + (-1)^\ell \langle \phi_0 | \phi_{\frac{N}{2}} \rangle.$$

Defining

$$s_n = \langle \phi_j | \phi_{j+n} \rangle$$

and

$$h_n = \langle \phi_j | \mathcal{H} | \phi_{j+n} \rangle$$

we obtain

$$\langle \Psi_\lambda | \Psi_\lambda \rangle = s_0 + 2s_1 \cos\left(\frac{2\pi}{N} \ell\right) + 2s_2 \cos\left(\frac{2\pi}{N} 2\ell\right) + \dots + s_{\frac{N}{2}} \cos(\pi\ell)$$

and

$$\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle = h_0 + 2h_1 \cos\left(\frac{2\pi}{N} \ell\right) + 2h_2 \cos\left(\frac{2\pi}{N} 2\ell\right) + \dots + h_{\frac{N}{2}} \cos(\pi\ell).$$

Assuming (as a somewhat crude simplification) that $s_i = 0$ for $i \geq 1$ and $h_i = 0$ for $i \geq 2$, and noting that $s_0 = \langle \phi_i | \phi_i \rangle = 1$, we obtain

$$E_\ell = \frac{\langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle}{\langle \Psi_\lambda | \Psi_\lambda \rangle} \approx h_0 + 2h_1 \cos\left(\frac{2\pi}{N}\ell\right).$$

Defining $\epsilon_0 = h_0$, $t = -h_1$, and $k = \frac{2\pi}{L}\ell$ we obtain

$$E_\ell = \epsilon_0 - 2t \cos(ka).$$

This is equation (11.6) in Simon's textbook.

5. Simon, Chapter 11.4: Two basis functions in each unit cell

Here we consider the treatment of a system in which the (translational) symmetry is not sufficient to determine the wave functions completely. The idea developed in Section 1.2 is applied.

Let there be two basis functions, ϕ_j and ψ_j , in each unit cell.

This covers the following situations:

1. Each atom has two energy levels.
2. There are two distinct atoms in each unit cell.
3. The two atoms in each unit cell are identical, but the distances between neighboring atoms alternate (Peierls Distortion).

We construct two sets of eigenfunctions of \hat{T} :

$$\Phi_\lambda = \frac{1}{\sqrt{N}} \sum_{j=1}^N \lambda^{-j} \phi_j,$$

and

$$\Psi_\lambda = \frac{1}{\sqrt{N}} \sum_{j=1}^N \lambda^{-j} \psi_j.$$

First we note that for $\lambda \neq \lambda'$

$$\langle \Phi_\lambda | \Psi_{\lambda'} \rangle = 0 \quad \text{why?}$$

and

$$\langle \Phi_\lambda | \mathcal{H} | \Psi_{\lambda'} \rangle = 0. \quad \text{why?}$$

We now apply the variational principle. We need to evaluate

$$S_{\phi,\phi} = \langle \Phi_\lambda | \Phi_\lambda \rangle$$

$$S_{\phi,\psi} = \langle \Phi_\lambda | \Psi_\lambda \rangle$$

$$S_{\psi,\psi} = \langle \Psi_\lambda | \Psi_\lambda \rangle$$

and

$$H_{\phi,\phi} = \langle \Phi_\lambda | \mathcal{H} | \Phi_\lambda \rangle$$

$$H_{\phi,\psi} = \langle \Phi_\lambda | \mathcal{H} | \Psi_\lambda \rangle$$

$$H_{\psi,\psi} = \langle \Psi_\lambda | \mathcal{H} | \Psi_\lambda \rangle,$$

and solve the 2×2 generalized eigenvalue problem

$$\begin{vmatrix} H_{\phi,\phi} - ES_{\phi,\phi} & H_{\phi,\psi} - ES_{\phi,\psi} \\ H_{\psi,\phi} - ES_{\psi,\phi} & H_{\psi,\psi} - ES_{\psi,\psi} \end{vmatrix} = 0$$

for each λ . Note that $S_{\psi,\phi} = S_{\phi,\psi}^*$ and $H_{\psi,\phi} = H_{\phi,\psi}^*$.

Since there are two eigenvalues for each allowed value of λ , we obtain two bands, with N energies in each. The ranges of energies of these two bands will either overlap or not, depending on the values of the various matrix elements.

As an obvious generalization of the procedure described for the case of a single orbital per unit cell, the matrix elements specified above can be evaluated as follows.

$$S_{\phi,\phi} = s_{\phi_1,\phi_1} + 2s_{\phi_1,\phi_2} \cos\left(\frac{2\pi}{N}\ell\right) + 2s_{\phi_1,\phi_3} \cos\left(\frac{2\pi}{N}2\ell\right) + \cdots + s_{\phi_1,\phi_{\frac{N}{2}}} \cos(\pi\ell),$$

$$S_{\phi,\psi} = s_{\phi_1,\psi_1} + 2s_{\phi_1,\psi_2} \cos\left(\frac{2\pi}{N}\ell\right) + 2s_{\phi_1,\psi_3} \cos\left(\frac{2\pi}{N}2\ell\right) + \cdots + s_{\phi_1,\psi_{\frac{N}{2}}} \cos(\pi\ell),$$

$$S_{\psi,\psi} = s_{\psi_1,\psi_1} + 2s_{\psi_1,\psi_2} \cos\left(\frac{2\pi}{N}\ell\right) + 2s_{\psi_1,\psi_3} \cos\left(\frac{2\pi}{N}2\ell\right) + \cdots + s_{\psi_1,\psi_{\frac{N}{2}}} \cos(\pi\ell),$$

and

$$H_{\phi,\phi} = h_{\phi_1,\phi_1} + 2h_{\phi_1,\phi_2} \cos\left(\frac{2\pi}{N}\ell\right) + 2h_{\phi_1,\phi_3} \cos\left(\frac{2\pi}{N}2\ell\right) + \cdots + h_{\phi_1,\phi_{\frac{N}{2}}} \cos(\pi\ell),$$

$$H_{\phi,\psi} = h_{\phi_1,\psi_1} + 2h_{\phi_1,\psi_2} \cos\left(\frac{2\pi}{N}\ell\right) + 2h_{\phi_1,\psi_3} \cos\left(\frac{2\pi}{N}2\ell\right) + \cdots + h_{\phi_1,\psi_{\frac{N}{2}}} \cos(\pi\ell),$$

$$H_{\psi,\psi} = h_{\psi_1,\psi_1} + 2h_{\psi_1,\psi_2} \cos\left(\frac{2\pi}{N}\ell\right) + 2h_{\psi_1,\psi_3} \cos\left(\frac{2\pi}{N}2\ell\right) + \cdots + h_{\psi_1,\psi_{\frac{N}{2}}} \cos(\pi\ell).$$

Here, $s_{\phi_1,\phi_k} = \langle \phi_1 | \phi_k \rangle$, $h_{\phi_1,\phi_k} = \langle \phi_1 | \mathcal{H} | \phi_k \rangle$, etc.

To simplify the remaining computations it is convenient to distinguish among the three types of problems specified above, and assume that, in each case, *only certain matrix elements*, in the atomic basis, *do not vanish*.

1. When each atom has two energy levels the non-vanishing matrix elements are taken to be

$$\langle \phi_j | \phi_j \rangle = 1, \quad \langle \psi_j | \psi_j \rangle = 1,$$

and

$$\begin{aligned} \langle \phi_j | \mathcal{H} | \phi_j \rangle &= \epsilon_A, & \langle \psi_j | \mathcal{H} | \psi_j \rangle &= \epsilon_B, \\ \langle \phi_j | \mathcal{H} | \phi_{j+1} \rangle &= t_{A,A}, & \langle \phi_j | \mathcal{H} | \psi_{j+1} \rangle &= t_{A,B}, & \langle \psi_j | \mathcal{H} | \psi_{j+1} \rangle &= t_{B,B}. \end{aligned}$$

In this case, $S_{\phi,\phi} = S_{\psi,\psi} = 1$, $S_{\phi,\psi} = 0$, and

$$H_{\phi,\phi} = \epsilon_A + 2t_{A,A} \cos\left(\frac{2\pi}{N}\ell\right)$$

$$H_{\phi,\psi} = 2t_{A,B} \cos\left(\frac{2\pi}{N}\ell\right)$$

$$H_{\psi,\psi} = \epsilon_B + 2t_{B,B} \cos\left(\frac{2\pi}{N}\ell\right).$$

In Simon's Question (11.4a) the further assumption $t_{A,B} = 0$ is made, reducing this problem to a superposition of two non-interacting single-orbital dispersion relations. This simplification is relaxed in (11.4b).

2. There are two distinct atoms in each unit cell:

$$\langle \phi_j | \phi_j \rangle = 1, \quad \langle \psi_j | \psi_j \rangle = 1$$

and

$$\langle \phi_j | \mathcal{H} | \phi_j \rangle = \epsilon_A, \quad \langle \psi_j | \mathcal{H} | \psi_j \rangle = \epsilon_B, \quad \langle \phi_j | \mathcal{H} | \psi_j \rangle = t_{A,B}, \quad \langle \psi_j | \mathcal{H} | \phi_{j+1} \rangle = t_{B,A}.$$

In Simon's textbook, problem 11.2, the further simplification $t_{A,B} = t_{B,A}$ is made.

3. The two atoms in each unit cell are identical, but the distances between neighboring atoms alternate (Peierls Distortion).

This case differs from case 2 by the fact that $\epsilon_A = \epsilon_B$ but $t_{A,B} \neq t_{B,A}$.

6. Simon, Chapter 15: Nearly free electrons in a periodic potential

Here we use perturbation theory to investigate the effect of a weak periodic potential on electrons that are otherwise free. We apply the ideas presented in Section 1.3.

Free electrons in one dimension can be described by the wave functions $|k\rangle = \exp(ikx)$. These functions are eigenfunctions of the momentum operator $\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$ with the eigenvalue $\hbar k$. Moreover, $|k\rangle$ is an eigenfunction of the kinetic energy operator $\mathcal{H}_0 = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$, with the eigenvalue $\frac{(\hbar k)^2}{2m}$. In the presence of a periodic potential with lattice constant a ,

$$V(x+a) = V(x)$$

we introduce the translation operator \hat{T} , defined by

$$\hat{T}f(x) = f(x+a),$$

and the periodic boundary condition

$$\hat{T}^N f(x) = f(x+Na) = f(x),$$

where N is some integer that we may eventually take to be arbitrarily large. We will now show that the periodic boundary condition splits the complete pertinent Hilbert space into N subspaces, specified by the distinct eigenvalues of \hat{T} . We note that

$$\hat{T}|k\rangle = \hat{T} \exp(ikx) = \exp(ik(x+a)) = \exp(ika) \exp(ikx) = \exp(ika)|k\rangle.$$

The periodic boundary condition implies that $\hat{T}^N = \hat{I}$, where \hat{I} is the identity operator. Hence, $\exp(ikNa) = 1$ or $k = \frac{2\pi n}{Na}$, where $n = 0, \pm 1, \pm 2, \dots$. Two eigenfunctions that correspond to quantum numbers n and n' that differ by N (or an integer multiple of N) have wave vectors k and k' , respectively, that differ by (an integer multiple of) $\frac{2\pi}{a}$. Hence, they correspond to a common eigenvalue $\exp(ika) = \exp(ik'a)$ of the translation operator. Specifically, the two eigenfunctions $\exp(-ikx)$ and $\exp(ikx)$, which correspond to the same kinetic energy, have the same eigenvalue with respect to \hat{T} if $k = n\frac{\pi}{a}$, where n is an integer.

Simon's chapter 15 proceeds by invoking first order perturbation theory. The zero order energy is the eigenfunction of the kinetic energy operator $\mathcal{H}_0 = \frac{\hat{p}^2}{2m}$, which for $|k\rangle$ is equal to $\frac{(\hbar k)^2}{2m}$. For $|k| < \frac{\pi}{a}$ the degeneracy of the function $\exp(ikx)$ with $\exp(-ikx)$ with respect to the zero order Hamiltonian can be disregarded, because they belong to distinct eigenvalues of \hat{T} , implying that the off-diagonal matrix-element $\langle -k|\mathcal{H}_0|k\rangle$ as well as the overlap integral (scalar product) $\langle -k|k\rangle$ vanish.

However, at $k_0 = \frac{\pi}{a}$ the two degenerate zero-order eigenfunctions of the Hamiltonian, $|k_0\rangle$ and $| -k_0\rangle$, are eigenfunctions of \hat{T} with the same eigenvalue, so degenerate first-order perturbation theory has to be invoked, *i. e.*, the matrix

$$\begin{pmatrix} \langle -k_0|V| -k_0\rangle & \langle -k_0|V|k_0\rangle \\ \langle k_0|V| -k_0\rangle & \langle k_0|V|k_0\rangle \end{pmatrix}$$

has to be diagonalized, yielding the zero-order wave functions and the corresponding first order energies.

Simon continues by inspecting the two wave functions $| -k_0 + \delta\rangle$ and $|k_0 + \delta\rangle$, that for small δ are nearly degenerate eigenfunctions of $\mathcal{H}_0 = -\frac{\hbar^2}{2m}$. These two wave functions have the same eigenvalue with respect to \hat{T} , hence a non-vanishing matrix element $\langle -k_0 + \delta|V|k_0 + \delta\rangle$. Simon constructs and diagonalizes a two by two matrix for these two wave functions, just like we did in the degenerate case. However, since these states are not strictly degenerate, a justification for constructing and diagonalizing the two by two matrix does not follow from perturbation theory. Generalizing this observation we note that all the functions of the form

$$\left\{ \exp\left(i\left(k + \frac{2\pi}{a}\ell\right)x\right) ; \ell = 0, \pm 1, \pm 2, \dots \right\}, \quad (6)$$

are eigenfunctions of \hat{T} with the same eigenvalue, $\exp(ika)$, hence, the matrix element of the Hamiltonian (specifically, the periodic potential) between any two of them does not need to vanish. Using these functions as a basis for a variational calculation we can, in principle, get exact eigenvalues (and eigenfunctions) of the Hamiltonian¹⁶. Realistically, we can only construct and diagonalize finite matrices, thereby obtaining an approximation (more precisely, an upper bound) of the low lying eigenvalues of the Hamiltonian. For k well below the zone boundary $k_0 = \frac{\pi}{a}$ the single basis function $\exp(ikx)$ may be sufficient, but as the zone boundary is approached at least the nearly degenerate wave function $\exp\left(i\left(k - \frac{2\pi}{a}\right)x\right)$ should be included along with $\exp(ikx)$, yielding the same two by two matrix that Simon

¹⁶The theory of the Fourier series, that you may have encountered in one of your math courses, tells us that the set specified by (6) is a complete set in the space of periodic functions of x with periodicity a .

constructed and diagonalized¹⁷.

7. Simon, Chapter 9: Translational symmetry and vibrational modes of the one-dimensional periodic lattice

The present section begins with a leisurely introduction of the concept of a normal mode of vibration, illustrated by investigating molecules that consist of a few atoms. We emphasize the use of symmetry, investigating the systems considered both classically (i. e., using Newtonian mechanics) and quantum mechanically. We then proceed to examine the oscillations of atoms on (one dimensional) lattices.

7.1 Introductory example: separation of the center-of-mass and relative motion of a two-particle system

The present subsection is a review of a problem you dealt with before. It should help to recall the idea of transforming the coordinates to make the Hamiltonian separable.

We begin by recalling the classical (Newtonian) treatment of two particles with masses m_1 and m_2 moving along the x axis. Denoting the positions of the two particles by x_1 and x_2 , respectively, we assume that they interact with one another via a potential that depends on the distance between them, $V(x_2 - x_1)$. Newton's equations of motion for the two particles can be written in the form

$$\begin{aligned} m_1 \frac{d^2 x_1}{dt^2} &= -\frac{\partial V}{\partial x_1} \\ m_2 \frac{d^2 x_2}{dt^2} &= -\frac{\partial V}{\partial x_2}. \end{aligned}$$

Since $\frac{\partial V}{\partial x_2} = -\frac{\partial V}{\partial x_1}$, it follows that

$$\frac{d^2(m_1 x_1 + m_2 x_2)}{dt^2} = 0,$$

suggesting that the center-of-mass coordinate $X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ moves with zero acceleration, like a free particle (with mass $M = m_1 + m_2$). Multiplying the equation of motion for x_1 by m_2 , the equation of motion for x_2 by m_1 , and subtracting the first from the second, we obtain

$$m_1 m_2 \frac{d^2(x_2 - x_1)}{dt^2} = -\left(m_1 \frac{\partial V}{\partial x_2} - m_2 \frac{\partial V}{\partial x_1}\right).$$

¹⁷A more careful analysis shows that the eigenvalues of this two by two matrix can be well-approximated by first order non-degenerate perturbation theory when the absolute value of the matrix element $\langle -k_0 + \delta | V | k_0 + \delta \rangle$ is small relative to the difference in the zero-order energies of $\exp(ikx)$ and $\exp\left(i\left(k - \frac{2\pi}{a}\right)x\right)$.

In terms of the relative coordinate $x = x_2 - x_1$ this equation becomes

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2 x}{dt^2} = - \frac{dV(x)}{dx}.$$

This equation looks like the equation of motion for a particle with mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ (the reduced mass).

We treated this two-particle system (that, for simplicity, we now confine to one dimension) in our Quantum Chemistry course. As above, the interaction depends only on the distance between the two particles, the Hamiltonian being

$$\mathcal{H} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial x_2^2} + V(x_2 - x_1). \quad (7)$$

Writing this Hamiltonian in terms of the center-of-mass coordinate

$$X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

and the relative coordinate,

$$x = x_2 - x_1,$$

we obtain

$$\mathcal{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V(x),$$

where $M = m_1 + m_2$ and $\mu = \frac{m_1 m_2}{m_1 + m_2}$. We discussed the three-dimensional counterpart of this transformation when we dealt with the hydrogen atom, where we denoted the mass of the nucleus by M and the mass of the electron by m . In that case, the reduced mass $\mu = \frac{mM}{M+m} = m \frac{1}{1+\frac{m}{M}} \approx m(1 - \frac{m}{M})$ is almost equal to the mass of the electron since $\frac{m}{M} \ll 1$. The small difference in the reduced mass accounts for most of the difference between the H and the D (deuterium) or T (tritium) spectral line frequencies.

The message of this section is that the separation of the center-of-mass motion is a consequence of the fact that the potential energy depends only on interparticle distances. When the system moves “as a rigid body”, $(x_1, x_2) = (X, X)$, then $|x_2 - x_1|$, which is the deviation of the interparticle distance from its equilibrium value, is not affected. This is easily generalized to any number of particles.

7.2 The harmonic approximation

The description of a system of masses that perform small oscillations relative to their fixed (equilibrium) points is considerably simplified if the interactions among the different masses are approximated by terms that are quadratic in the interparticle distances. This is what we mean by the harmonic approximation.

We consider a system of atoms, each performing small oscillations near a point in space (a lattice point). Recall that we are now at the second stage of the Born-Oppenheimer approximation: The Schroedinger equation for the motion of the electrons under the effect of stationary nuclei has been solved (at some acceptable level of approximation), yielding an electronic energy which depends on the nuclear coordinates. Since the nuclei are much heavier than the electrons, it is assumed that the electronic motions are much more rapid, so that at every nuclear geometry the electrons can be approximated by the solution of the electronic Schroedinger equations with nuclei that are at rest, at that geometry. The corresponding eigenvalue, that is commonly referred to as the electronic energy, is now used as the potential energy governing the motion of the nuclei. In practice it is quite common to approximate this potential energy by the analysis of spectroscopic data, but this is not an issue we wish to concern ourselves with here.

It is convenient to specify the location of each atom relative to the fixed lattice point that it corresponds to. Each atom interacts with the neighboring atoms. While the separation of the center-of-mass from the relative motions of the different atoms only depends on the property discussed in the previous section, further significant simplification is allowed if we can approximate the interactions by keeping only quadratic terms in the atomic coordinates, that we refer to as performing the harmonic approximation. This allows the construction of linear combinations of the atomic coordinates in such a way that the total potential energy of the system is a sum of squares of these linear combinations. These linear combinations are the **normal coordinates**. Once the transformation to normal coordinates has been achieved, we can treat the motion of each one of them separately, obtaining independent (non-interacting) oscillators, to which we refer as the **normal modes**.

The transformation into a separable set of coordinates can be carried out either within classical (Newtonian) mechanics or within quantum mechanics. The route via classical mechanics yields the normal modes and their frequencies (Ω). This can be completed by quantizing each normal mode, that is, specify the energy levels associated with it, $\hbar\Omega(n + \frac{1}{2})$. It is also possible to do everything quantum mechanically from the beginning. The final results are identical. We will see both procedures below.

The pertinent literature is somewhat implicit about (a polite way of saying “vague”) the fact that the independent normal modes can be described by two equivalent pictures. We can concentrate on the linear combinations of the atomic coordinates that yield a separable Hamiltonian, that we can refer to as the normal coordinates, each associated with its characteristic frequency. We can, equivalently, construct arrays of atomic coordinates that oscillate coherently, with a common frequency and well-defined phase relations. These two pictures are dual to one another, in a sense that will be explicated below. Each picture has worthwhile advantages, and both are discussed below.

7.3 The homonuclear diatomic molecule

This is the simplest application of the harmonic approximation. It should be familiar, but some ideas and definitions that will be useful later on are introduced. In particular, please pay attention to the two pictures of the normal modes, the

normal coordinate picture that emphasizes the form of the coordinates that allow separability of the Hamiltonian, vs. the atomic displacement arrays that clearly illustrate the coherent motions of the different atoms within each normal mode.

In a homonuclear diatomic molecule (a diatomic molecule that consists of two identical atoms) we have a single vibrational mode



We can use a similar diagram



to describe the center-of-mass motion, when the two atoms move in a common direction without changing the distance between them.

Allowing motion only along the x axis and assuming a harmonic interaction the Hamiltonian can be written in the form

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) + \frac{k}{2} (x_2 - x_1)^2 .$$

This is the harmonic approximation of the homonuclear counterpart ($m_1 = m_2$) of the Hamiltonian specified in equation (7). In terms of the center-of-mass and relative coordinates

$$X = \frac{1}{2}(x_1 + x_2) \quad \text{and} \quad x = x_2 - x_1$$

this Hamiltonian becomes

$$\mathcal{H} = \mathcal{H}_{\text{cm}} + \mathcal{H}_{\text{rel}} , \tag{8}$$

where

$$\mathcal{H}_{\text{cm}} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2}$$

is the center-of-mass Hamiltonian, and

$$\mathcal{H}_{\text{rel}} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{k}{2} x^2$$

is the Hamiltonian describing the relative motion (oscillation) of the two atoms. Here, $M = 2m$ is the total molecular mass and $\mu = \frac{m}{2}$ is the reduced mass.

Exercise: Please verify the form of equation (8).

The separability of the Hamiltonian into a sum of two terms that depend on distinct coordinates, as expressed by equation (8), implies that the eigenfunctions can be written as products of a free-particle wave function in terms of the center-of-mass coordinate, X , with energy $\frac{P^2}{2M}$, where P can obtain any (real) value, and a harmonic oscillator wave function in terms of the relative coordinate, x , with energy $\hbar\omega \left(n + \frac{1}{2} \right)$, where $\omega = \sqrt{\frac{k}{\mu}}$ and

$n = 0, 1, 2, \dots$.

We note in passing that this system could be treated classically. From Newton's second law, applied to each one of the atoms, we obtain

$$m \frac{d^2 x_1}{dt^2} = k(x_2 - x_1)$$

and

$$m \frac{d^2 x_2}{dt^2} = -k(x_2 - x_1).$$

Hence, the equation of motion for the center-of-mass coordinate is

$$\frac{d^2 X}{dt^2} = 0,$$

and the equation of motion for the relative coordinate is

$$m \frac{d^2 x}{dt^2} = -2kx.$$

The classical solution is $X = X_0 + vt$ where X_0 and v are two arbitrary constants (the initial position and the constant center-of-mass velocity), and $x = A \cos(\omega t + \phi)$, where $\omega = \sqrt{\frac{k}{\mu}}$ ($\mu = \frac{m}{2}$) while A and ϕ are two arbitrary constants (the amplitude and initial phase of the oscillation of x).

X and x are simple examples of **normal coordinates**. To obtain a more pictorial description of the mode of motion represented by X we note that taking $x = 0$ we obtain $x_1 = x_2 = X$, *i. e.* the two particles move together in space, whereas taking $X = 0$ we obtain $x_2 = -x_1 = \frac{x}{2}$, describing an oscillation of the two particles against one another. It is convenient to introduce the atomic displacement arrays $(x_1, x_2)_{\text{cm}} = (X, X)$, describing the center-of-mass motion (*i. e.*, both atoms shift by the same amount from their origins) and $(x_1, x_2)_{\text{rel}} = (-\frac{x}{2}, \frac{x}{2})$, describing the relative (oscillatory) mode of the atoms against one another.

The Hamiltonian, equation (7), is symmetric with respect to the transposition of particle 1 and particle 2. The transposition operator, $\hat{T}_{(1,2)}$, can be defined by its action on the atomic coordinates

$$\hat{T}_{(1,2)} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} x_2 \\ x_1 \end{pmatrix}.$$

Both X and x are eigenfunctions of this operator, *i. e.*,

$$\hat{T}_{(1,2)} \begin{pmatrix} X \\ x \end{pmatrix} = \hat{T}_{(1,2)} \begin{pmatrix} \frac{1}{2}(x_1 + x_2) \\ x_2 - x_1 \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(x_2 + x_1) \\ x_1 - x_2 \end{pmatrix} = \begin{pmatrix} X \\ -x \end{pmatrix}.$$

Hence, X is symmetric and x is antisymmetric under this operation. We note that x^2 is symmetric with respect to $\hat{T}_{(1,2)}$. This fact, together with the equality of the two masses,

lies at the heart of the relevance of the symmetry operation $\hat{T}_{(1,2)}$ to the transformation into normal modes, as the following examples will illustrate more powerfully. Comparison with the way the normal-mode coordinates were determined for the unsymmetric system considered in section 7.1 is instructive.

7.4 The linear triatomic molecule

For the system considered here the symmetry of the Hamiltonian is sufficient to determine the separable coordinates (the normal modes) completely. A similar situation will be encountered when we deal with the vibrations of identical atoms on a one-dimensional periodic lattice, in section 7.8.1

For a linear triatomic molecule (with identical atoms), confined to one-dimensional motion, we write the Hamiltonian in the form

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + \frac{k}{2} \left((x_2 - x_1)^2 + (x_3 - x_2)^2 \right). \quad (9)$$

We assumed that the potential energy is a sum of two quadratic nearest-neighbor interactions. This Hamiltonian commutes with the transposition operator, $\hat{T}_{(1,3)}$, defined via

$$\hat{T}_{1,3} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} x_3 \\ x_2 \\ x_1 \end{pmatrix}.$$

Starting from the atomic coordinates x_1, x_2 and x_3 we can construct a single antisymmetric linear combination, $x = x_3 - x_1$, but both $x_1 + x_3$ and x_2 are symmetric under the operation of $\hat{T}_{(1,3)}$. The linear combination $X = \frac{1}{3}(x_1 + x_2 + x_3)$ represents the center-of-mass coordinate. The center-of-mass mode corresponds to the atoms moving in a common direction, *i. e.*,

$$x_1 = x_2 = x_3 = X. \quad (10)$$

Clearly, the antisymmetric coordinate $x = x_3 - x_1$ vanishes if a motion that satisfies equation (10) takes place.

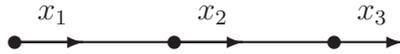
The linear combination $\tilde{x} = x_1 - 2x_2 + x_3$ of the two symmetric coordinates ($x_1 + x_3$ and x_2), is (obviously) symmetric as well. The relative coefficients of the symmetric basis functions $x_1 + x_3$ and x_2 were chosen so that \tilde{x} vanishes when rigid center-of-mass motion, as specified in equation (10), takes place.

Straightforward transformation yields

$$\begin{aligned} x_1 &= X - \frac{x}{2} + \frac{\tilde{x}}{6} \\ x_2 &= X - \frac{\tilde{x}}{3} \\ x_3 &= X + \frac{x}{2} + \frac{\tilde{x}}{6} \end{aligned}$$

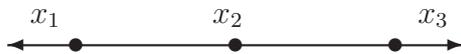
Once again, pure center-of-mass motion, corresponding to $x = 0$ and $\tilde{x} = 0$, is described by the atomic coordinate array $(x_1, x_2, x_3)_{\text{cm}} = (X, X, X)$, *i. e.*, all atoms move in the same direction. The vibrational mode \tilde{x} , which is symmetric with respect to $\hat{T}_{1,3}$, corresponds to $X = 0$ and $x = 0$ and is described by the atomic coordinate array $(x_1, x_2, x_3)_{\text{S}} = (\frac{\tilde{x}}{6}, -\frac{\tilde{x}}{3}, \frac{\tilde{x}}{6})$, *i. e.*, when atoms 1 and 3 move to the right by the same amount, atom 2 moves to the left by twice this amount. The antisymmetric mode x is described by the atomic coordinate array $(x_1, x_2, x_3)_{\text{a}} = (-\frac{x}{2}, 0, \frac{x}{2})$, *i. e.*, when atom 1 moves to the left atom 3 moves to the right by the same amount, and atom 2 stays in place.

Thus, the center-of-mass mode is



with all three atoms moving in the same direction.

The antisymmetric vibrational mode is



with the terminal atoms moving in opposite directions and the central atom standing still, and the symmetric vibrational mode is



with the terminal atoms moving in the same direction and the central atom moving in the opposite direction with twice the amplitude of the terminal atoms, keeping the center-of-mass at rest.

We note in passing that the symmetry properties of the linear triatomic molecule could be treated in alternative (but totally equivalent) ways. Instead of the operator $\hat{T}_{1,3}$, that permutes the particles 1 and 3, we could apply the operator of reflection through the plane which is perpendicular to the x axis, crossing it at the equilibrium position of particle 2. The action of this operator can be described by

$$\hat{\sigma} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} -x_3 \\ -x_2 \\ -x_1 \end{pmatrix}.$$

The center-of-mass and the \tilde{x} modes would be labelled as antisymmetric with respect to this operator, whereas the oscillation mode x , in which the central atom is at rest, would be labelled as symmetric.

So far we did not need to consider the Hamiltonian, except the fact that it commutes with $\hat{T}_{(1,3)}$. This fact was sufficient to determine the form of the normal coordinates, but we need to examine the dynamical properties of our system in order to determine the vibrational frequencies associated with the different normal modes. The potential energy assumed in equation (9) is

$$V = \frac{k}{2} \left((x_2 - x_1)^2 + (x_3 - x_2)^2 \right).$$

The center-of-mass coordinate corresponds to rigid motion of the molecule in space, with the distances between different atoms in the molecule remaining unchanged. It follows that the molecular potential energy cannot depend on the center-of-mass coordinate. Both x^2 and \tilde{x}^2 are symmetric under $\hat{T}_{1,3}$, so both can appear in the transformed expression for the potential energy. It is easy to verify that

$$\begin{aligned}\frac{x + \tilde{x}}{2} &= x_3 - x_2 \\ \frac{x - \tilde{x}}{2} &= x_2 - x_1\end{aligned}$$

so

$$\begin{aligned}V &= \frac{k}{2} \left((x_2 - x_1)^2 + (x_3 - x_2)^2 \right) \\ &= \frac{k}{2} \left(\left(\frac{x - \tilde{x}}{2} \right)^2 + \left(\frac{x + \tilde{x}}{2} \right)^2 \right) \\ &= \frac{k}{4} (x^2 + \tilde{x}^2) .\end{aligned}$$

The only other quadratic term is the mixed term $x\tilde{x}$, which is odd under $\hat{T}_{1,3}$. Since the potential is symmetric (even) under the operation of $\hat{T}_{(1,3)}$, this term cannot appear in the expression for the potential energy. Understanding this point is crucial to understanding the relevance of symmetry to the normal mode analysis.

At this point we can proceed either within classical (Newtonian) mechanics or within quantum mechanics. We will do both, and compare the results. Newton's equations for the three particles yield

$$\begin{aligned}m \frac{d^2 x_1}{dt^2} &= -\frac{dV}{dx_1} = k(x_2 - x_1) \\ m \frac{d^2 x_2}{dt^2} &= -\frac{dV}{dx_2} = k(x_1 - 2x_2 + x_3) \\ m \frac{d^2 x_3}{dt^2} &= -\frac{dV}{dx_3} = k(x_2 - x_3)\end{aligned}$$

Exercise: Please verify that the classical equations of motion for the normal coordinates X , x , and \tilde{x} are

$$\begin{aligned}\frac{d^2 X}{dt^2} &= 0 \\ m \frac{d^2 x}{dt^2} &= -kx \\ m \frac{d^2 \tilde{x}}{dt^2} &= -3k\tilde{x}\end{aligned}$$

Exercise: Please write the classical expressions for the time-dependence of the three coordinates X , x , and \tilde{x} .

To treat the Hamiltonian (9) quantum mechanically we express the kinetic energy in terms of the normal coordinates, obtaining, after some straightforward analysis,

$$\mathcal{H} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2\tilde{\mu}} \frac{\partial^2}{\partial \tilde{x}^2} + \frac{k}{4} (x^2 + \tilde{x}^2). \quad (11)$$

where $M = 3m$, $\mu = \frac{m}{2}$, and $\tilde{\mu} = \frac{m}{6}$.

Exercise: Please verify that for an eigenfunction of the Hamiltonian (11) the energy is

$$E = \frac{P^2}{2M} + \hbar\omega \left(n + \frac{1}{2} \right) + \hbar\tilde{\omega} \left(\tilde{n} + \frac{1}{2} \right),$$

where P is the (arbitrary) center-of-mass momentum, $\omega = \sqrt{\frac{k}{m}}$, and $\tilde{\omega} = \sqrt{\frac{3k}{m}}$. n and \tilde{n} are the quantum numbers of the two vibrational modes.

Exercise: Please replace the potential energy in equation (9) by

$$V = \frac{k}{2} \left((x_2 - x_1)^2 + (x_3 - x_2)^2 \right) + \frac{\kappa}{2} (x_3 - x_1)^2.$$

The additional term describes an interaction between atoms 1 and 3. You may expect that $\kappa < k$.

Please verify that this potential is still symmetric with respect to $\hat{T}_{(1,3)}$. It follows that the normal modes are the same as above.

Please express the modified potential in terms of the normal coordinates and derive the frequencies that correspond to the two vibrational modes. You may use either the classical or the quantum formalism, or both.

7.5 The linear tetraatomic molecule

For the system considered here the symmetry of the Hamiltonian is not sufficient to determine the normal modes completely. The same situation will be encountered in section 7.8.2 for periodic lattices with more than one atom in each unit cell.

A realistic example is $O = C = C = O$, but we shall assume four equal masses and three equal harmonic force constants between any two neighbors. Allowing motion only along the molecular axis we denote the atomic displacements by x_1, x_2, x_3, x_4 , and write the potential energy in the form

$$V = \frac{k}{2} \left((x_2 - x_1)^2 + (x_3 - x_2)^2 + (x_4 - x_3)^2 \right) \quad (12)$$

Clearly, the permutation $\hat{T}_{14,23}$, defined by

$$\hat{T}_{14,23} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{pmatrix} = \begin{pmatrix} x_4 \\ x_3 \\ x_2 \\ x_1 \end{pmatrix},$$

is a symmetry operator, under which the potential (as well as the kinetic) energy is invariant. Since $\hat{T}_{14,23}^2 = 1$, this symmetry operator has two eigenvalues, 1 and -1. Two eigenfunctions, $x_1 + x_4$ and $x_2 + x_3$, correspond to the first eigenvalue, and two eigenfunctions, $x_a = x_1 - x_4$ and $x_b = x_2 - x_3$, correspond to the second. We will use the term ‘‘symmetry coordinates’’ to describe linear combinations of atomic displacements, such as $x_1 + x_4$, $x_2 + x_3$ as well as x_a and x_b , that are eigenfunctions of the symmetry operator. This means that all four linear combinations were determined by referring to the symmetry operator $\hat{T}_{14,23}$, and should not be confused with the fact that the first two are symmetric and the other two are antisymmetric with respect to this operator.

Since the center-of-mass coordinate, $X = \frac{1}{4}(x_1 + x_2 + x_3 + x_4)$, is a linear combination of the two symmetric coordinates $x_1 + x_4$ and $x_2 + x_3$, we can immediately write the symmetric internal coordinate as $x_s = x_1 - x_2 - x_3 + x_4$. On the other hand, concerning the antisymmetric normal modes the symmetry analysis only allows us to say that they are linear combinations of x_a and x_b . The potential, equation (12), must be a linear combination of x_s^2 , x_a^2 , x_b^2 and $x_a x_b$, which are the only quadratic terms that are symmetric with respect to $\hat{T}_{14,23}$. It is a simple exercise to show that

$$V = \frac{k}{2} \left(\frac{x_s^2}{2} + \frac{x_a^2}{2} + \frac{3x_b^2}{2} - x_a x_b \right).$$

To fully separate the two antisymmetric modes we have to carry out full dynamical analysis, that will yield the vibrational frequencies as well. This can be done either classically or quantum mechanically. We choose to start by expressing the (quantum mechanical) kinetic energy operator in terms of the coordinates X , x_s , x_a and x_b . Application of the chain rule (repeatedly) yields

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} + \frac{\partial^2}{\partial x_4^2} \right) = -\frac{\hbar^2}{2(4m)} \frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2(\frac{m}{4})} \frac{\partial^2}{\partial x_s^2} - \frac{\hbar^2}{2(\frac{m}{2})} \left(\frac{\partial^2}{\partial x_a^2} + \frac{\partial^2}{\partial x_b^2} \right).$$

It is easy to understand that the mixed second derivative $\frac{\partial^2}{\partial x_a \partial x_b}$ cannot appear in the expression for the kinetic energy. This follows from the fact that x_a depends only on x_1 and x_4 , whereas x_b depends only on x_2 and x_3 , so if we express the mixed second derivative $\frac{\partial^2}{\partial x_a \partial x_b}$ in terms of the atomic coordinates we will obtain terms such as $\frac{\partial^2}{\partial x_1 \partial x_2}$, that do not appear in the original expression for the kinetic energy operator.

Inspecting the terms that contain x_a and x_b in the kinetic energy operator we define $x_u = ax_a + bx_b$ and $x_v = bx_a - ax_b$, where $a^2 + b^2 = 1$. This transformation is a rotation in the (x_a, x_b) plane, since $x_u^2 + x_v^2 = x_a^2 + x_b^2$. We find that

$$-\frac{\hbar^2}{2(\frac{m}{2})} \left(\frac{\partial^2}{\partial x_a^2} + \frac{\partial^2}{\partial x_b^2} \right) = -\frac{\hbar^2}{2(\frac{m}{2})} \left(\frac{\partial^2}{\partial x_u^2} + \frac{\partial^2}{\partial x_v^2} \right),$$

So the kinetic energy operator remains separable in terms of the rotated antisymmetric coordinates. a (and b) are determined by writing the potential in terms of the new coordinates x_u and x_v , and demanding the coefficient of the mixed term, $x_u x_v$, to vanish. We obtain

$a = \sqrt{\frac{1}{2} \left(1 + \frac{\sqrt{2}}{2}\right)}$ and $b = \sqrt{\frac{1}{2} \left(1 - \frac{\sqrt{2}}{2}\right)}$, or, finally,

$$V = \frac{k}{2} \left(\frac{x_s^2}{2} + \frac{x_a^2}{2} + \frac{3x_b^2}{2} - x_a x_b \right) = \frac{k}{2} \left(\frac{x_s^2}{2} + \left(1 - \frac{\sqrt{2}}{2}\right) x_u^2 + \left(1 + \frac{\sqrt{2}}{2}\right) x_v^2 \right).$$

It follows that the frequencies associated with the three vibrational normal modes are $\Omega_s = \omega\sqrt{2}$, $\Omega_u = \omega\sqrt{2 - \sqrt{2}}$ and $\Omega_v = \omega\sqrt{2 + \sqrt{2}}$, where $\omega = \sqrt{\frac{k}{m}}$.

Alternatively, we treat the linear tetraatomic molecule via the Newtonian equations of motion

$$\begin{aligned} m \frac{d^2 x_1}{dt^2} &= k(x_2 - x_1) \\ m \frac{d^2 x_2}{dt^2} &= k(x_1 + x_3 - 2x_2) \\ m \frac{d^2 x_3}{dt^2} &= k(x_2 + x_4 - 2x_3) \\ m \frac{d^2 x_4}{dt^2} &= k(x_3 - x_4) \end{aligned}$$

Taking the appropriate linear combinations of these equations of motion we obtain the equations of motion for the symmetry coordinates

$$\begin{aligned} \frac{d^2 X}{dt^2} &= 0 \\ m \frac{d^2 x_s}{dt^2} &= -2kx_s \\ m \frac{d^2 x_a}{dt^2} &= k(x_b - x_a) \\ m \frac{d^2 x_b}{dt^2} &= k(x_a - 3x_b) \end{aligned}$$

While the center-of-mass coordinate, X , and the symmetric normal coordinate x_s are now separated, we still need to take linear combinations of the last two equations, defining (as above) $x_u = ax_a + bx_b$ and $x_v = bx_a - ax_b$. We find, after some algebra, that

$$m \frac{d^2 x_u}{dt^2} = k \left[(2ab - a^2 - 3b^2)x_u + (b^2 + 2ab - a^2)x_v \right], \quad (13)$$

with a similar expression for $m \frac{d^2 x_v}{dt^2}$. Requiring the coefficient of x_v on the right hand side of equation (13) to vanish we obtain, as we did in the quantum mechanical treatment,

$$a = \sqrt{\frac{1}{2} \left(1 + \frac{\sqrt{2}}{2}\right)}, \quad b = \sqrt{\frac{1}{2} \left(1 - \frac{\sqrt{2}}{2}\right)} \quad \text{and} \quad \Omega_u = \omega\sqrt{2 - \sqrt{2}}.$$

7.6 On the use of symmetry to determine the normal modes

The illustrative few-atom examples considered above will now be used to motivate a more general statement about normal-mode analysis.

We consider N particles moving along the x axis, described by the Hamiltonian

$$\mathcal{H} = \sum_{j=1}^N \frac{\hat{p}_j^2}{2m} + V(x_1, x_2, \dots, x_N), \quad (14)$$

where m are the atomic masses.

The discussion of the two-particle system in section 7.1 suggested that separation of the center-of-mass coordinate is valid whenever the potential energy depends only on interparticle distances, and does not require the harmonic approximation. Assuming that the particles have a common mass, the center-of-mass coordinate is

$$\hat{X} = \frac{1}{N}(x_1 + x_2 + \dots + x_N).$$

Obviously, \hat{X} commutes for all the coordinates x_i , so it commutes with the potential $V(x_1, x_2, \dots, x_N)$. It follows that

$$\begin{aligned} [\mathcal{H}, \hat{X}] &= \frac{1}{2mN} \left[\sum_{j=1}^N \hat{p}_j^2, \sum_{j'=1}^N x_{j'} \right] \\ &= \frac{\hbar}{im} \frac{1}{N} (\hat{p}_1 + \hat{p}_2 + \dots + \hat{p}_N) = \frac{\hbar}{imN} \hat{P}, \end{aligned}$$

where we used the identity $[\hat{p}_j^2, x_{j'}] = 2\frac{\hbar}{i}\hat{p}_j\delta_{j,j'}$. \hat{P} , the total momentum of the center-of-mass, can be used to construct the unitary operator

$$\hat{U} = \exp\left(\frac{i}{\hbar}\alpha\hat{P}\right) = \prod_{i=1}^N \exp\left(\frac{i}{\hbar}\alpha\hat{p}_i\right).$$

that, upon acting on a function of the coordinates, $f(x_1, x_2, \dots, x_N)$ translates it into $f(x_1 + \alpha, x_2 + \alpha, \dots, x_N + \alpha)$.

Exercise: Please prove that $\exp\left(\frac{i}{\hbar}\alpha\hat{p}\right)f(x) = f(x + \alpha)$. [See footnote 13 for a hint].

If $f(x_1, x_2, \dots, x_N)$ depends only on interparticle distances, $x_i - x_j$, then it is invariant under the action of \hat{U} . The potential energy introduced in equation (14) satisfies this property, which is equivalent to $[\mathcal{H}, \hat{P}] = 0$. It follows that the eigenfunctions of the Hamiltonian can be written as products of eigenfunctions of \hat{P} (constant momentum motions of the center-of-mass) and functions of the internal coordinates. From now on we assume that the center-of-mass motion was separated, and we take $x_1 + x_2 + \dots + x_N = 0$.

Assuming that the N particle coordinates specify small deviations from the equilibrium positions of these particles we expand the potential in a multiple Taylor series in these

coordinates. Since the potential attains its minimum at the equilibrium positions of the particles, all the linear terms in the particle coordinates vanish. Invoking the harmonic approximation, we retain only quadratic terms (either of type x_i^2 or of type $x_i x_j$).

If the lattice has some symmetry properties (such as translational symmetry) then the Hamiltonian commutes with the corresponding symmetry operators. We can construct a set of N linear combinations of the atomic coordinates, each of which is an eigenfunction of these (commuting¹⁸) symmetry operators. We shall refer to these linear combinations as **symmetry coordinates**. It turns out that it is easier to construct eigenfunctions of the symmetry operators than to directly construct the normal coordinates, in terms of which the Hamiltonian is separable, so this is where we start.

In the simplest case we will obtain just one symmetry coordinate for each eigenvalue of the symmetry operator, which “automatically” solves our problem, serving as a normal coordinate [this is what we encountered when we discussed the linear triatomic molecule in section 7.4, and what happens in a lattice of identical atoms, that we treat next]. The reason is that if we express the (harmonic) potential in terms of these symmetry coordinates then each term should commute with the symmetry operator (or operators). The square of a symmetry coordinate that corresponds to the eigenvalue 1 or -1 of the symmetry operator is indeed totally symmetric. The symmetry operators that we shall encounter satisfy the property $\hat{O}^n = \hat{I}$, where \hat{I} is the identity operator (the operator that keeps any function that it acts on unchanged). n is an integer, which is sometimes called the order of the operator \hat{O} . The eigenvalues of \hat{O} must satisfy $\lambda^n = 1$ or $\lambda = \exp\left(i\frac{2\pi}{n}\ell\right)$; $\ell = 0, 1, 2, \dots, n-1$. To obtain totally-symmetric quadratic terms we consider products of symmetry coordinates of the form $x_\lambda x_{\lambda^*}$, since the action of the symmetry operator on this product produces the eigenvalue $\lambda\lambda^*$, which is equal to unity.

If we obtain more than one symmetry coordinate corresponding to the same eigenvalue of the symmetry operator then the solutions of our dynamical problem (the expressions for the normal coordinates in terms of which our Hamiltonian is separable) can be expressed as linear combinations of these degenerate symmetry coordinates [this is what we did when we studied the two symmetric modes of the tetraatomic molecule in section 7.5 and what we do below, dealing with a lattice of diatomic molecules].

All this will become much clearer below, as we consider concrete applications.

7.7 One dimensional atomic lattice (with periodic boundary conditions)

The treatment of the vibrational modes of atoms on a lattice is introduced.

We consider identical atoms arranged on a one-dimensional lattice. m is the mass of each atom and a is the distance between neighboring atoms. The lattice points, on the x axis, are at aj , where $j = \dots, -3, -2, -1, 0, 1, 2, 3, \dots$.

¹⁸the treatment of symmetry operators that do not commute with one another leads to very interesting further consequences that you can learn about in a decent course of group theory.

Let x_j denote the distance between the actual (momentary) position of atom j and its equilibrium position, at the lattice point. We shall refer to x_j as the atomic displacement coordinate. Assuming that there are only harmonic interactions between neighboring atoms, that can be written in the form $\frac{k}{2}(x_{j+1} - x_j)^2$, the total potential energy is

$$V = \frac{k}{2} \sum_{j=1}^N (x_{j+1} - x_j)^2$$

with the periodic boundary condition $x_{N+1} = x_1$. The force acting on atom ℓ is

$$F_\ell = -\frac{\partial V}{\partial x_\ell} = -k \left((x_\ell - x_{\ell-1}) - (x_{\ell+1} - x_\ell) \right) = k(x_{\ell-1} + x_{\ell+1} - 2x_\ell).$$

The equations of motion (Newton's second law) yield

$$k(x_{\ell-1} + x_{\ell+1} - 2x_\ell) = m \frac{\partial^2 x_\ell}{\partial t^2}. \quad (15)$$

At this stage the typical textbook treatment proceeds by introducing an “ansatz” (educated guess) concerning the atomic coordinate x_j , writing $x_j = x_0 \exp(i\Omega t - ika_j)$ [1, 2, 3, 4, 5, 6, 7, 8]. This ansatz consists of a time-dependent factor that can be easily justified by the notion of a “normal mode”, in which all atoms oscillate at a common frequency (although the feasibility of such normal modes has yet to be established), and a factor that depends on the location of the j 'th atom on the lattice, which remains to be justified by the results. The path towards these results using the translational symmetry is now clear.

7.8 Lattice translational symmetry: the atomic displacements picture

In the present subsection we use the translational symmetry of a one-dimensional lattice of oscillating atoms, with periodic boundary conditions, to derive the expressions for the coherent motions of the atoms within each normal mode. The result is identical with Simon's “ansatz”.

In our treatment of the motions of the nuclei in the triatomic and tetraatomic (linear) molecules, within the harmonic approximation, we learnt about the possibility to separate the motion into non-interacting normal modes. In the classical (Newtonian) framework each normal mode corresponds to a collective oscillation of all the atoms in the system, with a common frequency and specific phase relations. The natural way to describe each normal mode is by an array of atomic displacements (from the corresponding equilibrium positions), (x_1, x_2, \dots) . All the atomic displacements within such an array share a common time-dependent factor, $\exp(i\Omega t)$, and they are related by some characteristic “phase factors” that we derive below, temporarily denoting by Λ_ℓ . Hence,

$$x_\ell = x_0 \Lambda_\ell \exp(i\Omega t).$$

We shall refer to the description of the normal modes in terms of such atomic displacement arrays as the **atomic displacement picture**.

The normal modes can also be described by means of appropriate linear combinations of the atomic displacements. These linear combinations allow the Hamiltonian to be written as a sum of independent terms. Each independent term describes a harmonic oscillator expressed by one of these linear combinations of the atomic displacements. The frequencies of these harmonic oscillators are the same as the common frequencies of the atomic displacements in the arrays described above. We shall refer to this description as the **normal coordinate picture**.

The two pictures are entirely equivalent and it is easy to obtain the solution in terms of one of them from the solution in terms of the other. They emphasize different aspects of the problem. Different authors prefer one of the two pictures, usually not being very explicit about the existence of the other. I hope that you will find that being explicitly introduced to both (and to the relation between them) leads to a clearer understanding.

We treat the one-dimensional lattice in terms of the atomic displacements picture in the present section, and in terms of the normal coordinates picture in the following section.

7.8.1 The monoatomic lattice

In the case treated here the translational symmetry is sufficient to determine the normal modes (in the atomic displacement picture) completely.

We now describe a treatment that allows the “ansatz” quoted above to be naturally derived. We adhere to the specification of the states of the system by the array of atomic displacements,

$$(x_1, x_2, \dots, x_N),$$

satisfying the periodic boundary conditions $x_{j+N} = x_j$; $j = 1, 2, \dots, N$. We define the translation operator \hat{T} via $\hat{T}x_j = x_{j+1}$. Hence,

$$\hat{T}(x_1, x_2, \dots, x_{N-1}, x_N) = (x_2, x_3, \dots, x_N, x_1), \quad (16)$$

and

$$\hat{T}^N(x_1, x_2, \dots, x_{N-1}, x_N) = (x_1, x_2, \dots, x_{N-1}, x_N). \quad (17)$$

We now consider arrays of atomic displacements that satisfy

$$\hat{T}(x_1, x_2, \dots, x_{N-1}, x_N)_\lambda = \lambda(x_1, x_2, \dots, x_{N-1}, x_N)_\lambda, \quad (18)$$

that we shall refer to as eigen-arrays. It follows from equation (17) that $\lambda^N = 1$, hence,

$$\lambda = \exp\left(i\frac{2\pi}{N}\ell\right), \quad \text{where } \ell = 0, 1, \dots, N-1,$$

or, equivalently, $\ell = -\frac{N}{2} + 1, -\frac{N}{2} + 2, \dots, \frac{N}{2}$.

Comparing equations (16) and (18) we obtain

$$x_{j+1} = \lambda x_j \quad ; \quad j = 1, 2, \dots, N,$$

or $x_j = x_0 \lambda^j$.

The equations of motion (15) can be written in the form

$$\frac{\partial^2 x_j}{\partial t^2} = -\omega^2 (2x_j - x_{j-1} - x_{j+1}) = -\omega^2 \left(2x_j - \frac{1}{\lambda} x_j - \lambda x_j \right) = -\Omega_\lambda^2 x_j,$$

where $\omega^2 = \frac{k}{m}$ and

$$\Omega_\lambda^2 = \omega^2 \left(2 - \lambda - \frac{1}{\lambda} \right) = \omega^2 \left(2 - 2 \cos \left(\frac{2\pi}{N} \ell \right) \right) = 4\omega^2 \sin^2 \left(\frac{\pi}{N} \ell \right).$$

The time-dependent factor of the solution immediately follows as $\exp(\pm i\Omega_\lambda t)$.

As an example we note that, for even N , the highest frequency mode, that corresponds to $\ell = \frac{N}{2}$, yields $\lambda = -1$ and $\Omega = 2\omega$. The corresponding eigen-array is

$$(x_1, -x_1, x_1, -x_1, \dots, x_1, -x_1)_{-1},$$

where the index -1 is the eigenvalue of \hat{T} that characterizes this eigen-array.

It is a simple exercise in freshman mechanics to show that two rigid bodies, each consisting of $\frac{N}{2}$ masses on a circle, bound by harmonic springs, oscillate relative to one another at the frequency 2ω . As an additional example consider $\ell = \pm \frac{N}{4}$, yielding $\lambda = \pm i$, or the two degenerate normal modes specified by the arrays $(x_1, 0, -x_1, 0, \dots)$ and $(0, x_1, 0, -x_1, \dots)$. The corresponding frequency is $\Omega = \omega\sqrt{2}$. Here, again, the freshman mechanics counterpart is easy (and useful) to envision.

7.8.2 The one-dimensional diatomic lattice

In the case treated here the translational symmetry is not sufficient to determine the normal modes (in the atomic displacement picture) completely, but it still provides a significant simplification.

The coordinates of the two (distinct) atoms, with masses m and M , respectively, in the j 'th unit cell are x_j and y_j , respectively, both of them on the same (x) axis.

The potential energy is

$$V = \frac{k}{2} \sum_{j=1}^N (x_{j+1} - y_j)^2 + \frac{K}{2} \sum_{j=1}^N (y_j - x_j)^2,$$

with two distinct force constants, k and K . The Newtonian equations of motion (for the two atoms in the ℓ 'th unit cell are

$$\begin{aligned} m \frac{\partial^2 x_\ell}{\partial t^2} &= -\frac{\partial V}{\partial x_\ell} = -k(x_\ell - y_{\ell-1}) + K(y_\ell - x_\ell) \\ M \frac{\partial^2 y_\ell}{\partial t^2} &= -\frac{\partial V}{\partial y_\ell} = k(x_{\ell+1} - y_\ell) - K(y_\ell - x_\ell). \end{aligned}$$

When both $(x_1, x_2, \dots, x_N)_\lambda$ and $(y_1, y_2, \dots, y_N)_\lambda$ are eigen-arrays of \hat{T} with the same eigenvalue λ , we obtain

$$\begin{aligned} m \frac{\partial^2 x_\ell}{\partial t^2} &= -k(x_\ell - \frac{y_\ell}{\lambda}) + K(y_\ell - x_\ell) = -(k+K)x_\ell + \left(\frac{k}{\lambda} + K\right) y_\ell \\ M \frac{\partial^2 y_\ell}{\partial t^2} &= k(\lambda x_\ell - y_\ell) - K(y_\ell - x_\ell) = (k\lambda + K)x_\ell - (k+K)y_\ell, \end{aligned}$$

Assuming that all the atoms oscillate at the same frequency Ω we write $x_\ell(t) = x_\ell(0) \exp(i\Omega t)$ and $y_\ell(t) = y_\ell(0) \exp(i\Omega t)$, yielding

$$\begin{aligned} -m\Omega^2 x_\ell(0) &= -(k+K)x_\ell(0) + \left(\frac{k}{\lambda} + K\right) y_\ell(0) \\ -M\Omega^2 y_\ell(0) &= (k\lambda + K)x_\ell(0) - (k+K)y_\ell(0), \end{aligned}$$

or

$$\begin{pmatrix} \frac{k+K}{m} & -\frac{k}{\lambda} + K \\ -\frac{k\lambda+K}{M} & k+K \end{pmatrix} \begin{pmatrix} x_\ell(0) \\ y_\ell(0) \end{pmatrix} = \Omega^2 \begin{pmatrix} x_\ell(0) \\ y_\ell(0) \end{pmatrix}.$$

For $m = M$ the last matrix equation simplifies, and we obtain

$$\left(\frac{k+K}{m} - \Omega^2\right)^2 = \frac{1}{m^2} \left(\frac{k}{\lambda} + K\right) (k\lambda + K)$$

or

$$\Omega^2 = \frac{k+K}{m} \pm \frac{1}{m} \sqrt{k^2 + K^2 + kK \left(\lambda + \frac{1}{\lambda}\right)} = \frac{k+K}{m} \pm \frac{1}{m} \sqrt{(k-K)^2 + 4kK \cos^2\left(\frac{\pi}{N}\ell\right)}.$$

For $k = K$ this system reduces to the monoatomic one-dimensional lattice,

$$\Omega^2 = 2\omega^2 \left(1 \pm \cos\left(\frac{\pi}{N}\ell\right)\right) = 4\omega^2 \begin{cases} \sin^2\left(\frac{\pi}{2N}\ell\right) \\ \cos^2\left(\frac{\pi}{2N}\ell\right) \end{cases}$$

with period of length $2N$.

7.9 The normal coordinate picture: one dimensional atomic lattice

In the present subsection we introduce the application of the translational symmetry to construct the normal coordinates, that allow the Hamiltonian to be separated into a sum of non-interacting modes. We only consider the simplest case, in which symmetry solves the problem completely. This is, conceptually, a generalization of subsection 7.4. The more general case, in which the translational symmetry is not sufficient, can be dealt with using the idea illustrated in subsection 7.5.

Consider a linear combination of the atomic displacements x_1, x_2, \dots, x_N ,

$$X_\lambda = \sum_{j=1}^N c_j x_j,$$

which is an eigenfunction of \hat{T} , with some eigenvalue λ , i. e.,

$$\hat{T} X_\lambda = \lambda X_\lambda, \quad (19)$$

where

$$\lambda = \exp\left(i \frac{2\pi}{N} n\right) \quad ; \quad n = 0, 1, 2, \dots, N-1.$$

Denoting the length of the segment that contains N atoms by L we note that $L = Na$ so we can write

$$\lambda = \exp\left(i \frac{2\pi}{L} an\right).$$

$\frac{2\pi}{L}$ is the size of a unit cell in the (one dimensional) ‘‘reciprocal lattice’’. The set of points

$$\frac{2\pi}{L} n \quad ; \quad n = -\frac{N}{2}, -\frac{N}{2} + 1, \dots, \frac{N}{2} - 1$$

in this reciprocal lattice is referred to as **the first Brillouin zone**.

Equation (19) can be written in the form

$$\sum_{j=1}^N c_j x_{j+1} = \lambda \sum_{j=1}^N c_j x_j.$$

Here, $c_{N+1} = c_1$.

The left-hand side can be written as $\sum_{j=1}^N c_{j-1} x_j$ (understanding that $c_0 = c_N$), so $c_{j-1} = \lambda c_j$, or $c_j = c_0 \lambda^{-j}$.

We obtain

$$X_\lambda = c_0 \sum_{j=1}^N \lambda^{-j} x_j = c_0 \sum_{j=1}^N \exp\left(-i \frac{2\pi}{L} anj\right) x_j. \quad (20)$$

Hence, the Newtonian equation of motion is

$$\frac{\partial^2 X_\lambda}{\partial t^2} = c_0 \sum_{j=1}^N \lambda^{-j} \frac{\partial^2 x_j}{\partial t^2} = c_0 \sum_{j=1}^N \lambda^{-j} \frac{k}{m} (x_{j-1} + x_{j+1} - 2x_j),$$

where we used equation (15).

Defining $\omega^2 = \frac{k}{m}$, the right-hand side of the last equation can be written as

$$c_0 \omega^2 \sum_{j=1}^N (\lambda^{-j+1} + \lambda^{-j-1} - 2\lambda^{-j}) x_j = c_0 \omega^2 (\lambda + \lambda^{-1} - 2) \sum_{j=1}^N \lambda^{-j} x_j = \omega^2 (\lambda + \lambda^{-1} - 2) X_\lambda.$$

It follows that

$$\frac{\partial^2 X_\lambda}{\partial t^2} = -\omega^2(2 - \lambda - \lambda^{-1})X_\lambda, \quad (21)$$

i.e., X_λ is a normal coordinate with frequency

$$\begin{aligned} \Omega_\lambda &= \sqrt{\omega^2(2 - \lambda - \lambda^{-1})} = \omega \sqrt{2 - \exp\left(i\frac{2\pi}{N}n\right) - \exp\left(-i\frac{2\pi}{N}n\right)} \\ &= \omega \sqrt{2 - 2\cos\left(\frac{2\pi}{N}n\right)} = 2\omega \left| \sin\left(\frac{\pi}{N}n\right) \right| = 2\omega \left| \sin\left(\frac{\pi}{L}an\right) \right|. \end{aligned}$$

The solution of equation (21) is

$$\begin{aligned} X_\lambda(t) &= X_\lambda(0) \exp(\pm i\Omega_\lambda t) = c_0 \sum_{j=1}^N \exp\left(-i\frac{2\pi}{L}anj \pm i\Omega_\lambda t\right) x_j \\ &= c_0 \exp(\pm i\Omega_\lambda t) \sum_{j=1}^N \exp\left(-i\frac{2\pi}{L}anj\right) x_j, \end{aligned}$$

where we used equation (20).

The maximum frequency mode, $n = \frac{N}{2} = \frac{L}{2a}$, corresponds to $\lambda = \exp(-i\pi) = -1$, i. e., $X = x_1 - x_2 + x_3 - x_4 + \dots$: Each atom oscillates against the neighboring atom. Here we assumed that N is even.

Exercise: Please prove, directly, that the vibration frequency of such a mode is 2ω . Please describe the lowest frequency mode.

7.10 Relation between the normal coordinate and the atomic displacement pictures of the vibrational normal modes

The relation between the two pictures of a normal mode, the normal coordinate picture and the atomic displacements array picture, is explicitly worked out, showing that these two pictures are dual to one another, in a well-defined sense.

We saw above that the normal modes of vibration of a polyatomic molecule or of a system of atoms associated with a lattice can be described in two ways that appear to be distinct. The description which is easier to visualize involves an array of atomic displacements relative to the molecular or lattice equilibrium positions of the various atoms. The atomic displacements that comprise a normal mode oscillate with some common frequency, and they are related to one another by some characteristic phase relations. The other description emphasizes the role of the normal modes as separable coordinates. A normal mode is associated with a particular linear combination of the atomic displacements, that we refer to as the normal coordinate. If the Hamiltonian, in the harmonic approximation, is written in terms of the collection of normal coordinates, it separates into a sum of terms, each one

of which depends on a single normal coordinate. Each normal coordinate is associated with a frequency, which is identical with the frequency of a corresponding atomic displacements array. In the present section we wish to clarify the relation between the normal-coordinate picture and the atomic displacement picture, showing explicitly how the latter picture can be derived from the former.

We note that if only the mode X_λ is not at rest, and all the other $N - 1$ modes satisfy $X_{\lambda'} = 0$, where $\lambda' \neq \lambda$, then a solution of the set of N linear equations

$$\begin{cases} \lambda_1^{-1}x_1 + \lambda_1^{-2}x_2 + \lambda_1^{-3}x_3 + \cdots + \lambda_1^{-N}x_N = 0, \\ \lambda_2^{-1}x_1 + \lambda_2^{-2}x_2 + \lambda_2^{-3}x_3 + \cdots + \lambda_2^{-N}x_N = 0, \\ \vdots \\ \lambda_\ell^{-1}x_1 + \lambda_\ell^{-2}x_2 + \lambda_\ell^{-3}x_3 + \cdots + \lambda_\ell^{-N}x_N = c_\ell^{-1}X_\ell, \\ \vdots \\ \lambda_N^{-1}x_1 + \lambda_N^{-2}x_2 + \lambda_N^{-3}x_3 + \cdots + \lambda_N^{-N}x_N = 0, \end{cases} \quad (22)$$

yields $x_j = \frac{1}{N}\lambda_\ell^j X_{\lambda_\ell}$. To verify this solution we substitute the expressions for x_j in any of the $N - 1$ linear equations for $\lambda_i \neq \lambda_\ell$ and note that the equation is satisfied because

$$\lambda_i^{-1}\lambda_\ell + \lambda_i^{-2}\lambda_\ell^2 + \lambda_i^{-3}\lambda_\ell^3 + \cdots + \lambda_i^{-N}\lambda_\ell^N = 0.$$

The ℓ 'th equation is satisfied (if we choose $c_\ell^{-1} = 1$) because

$$\lambda_\ell^{-1}\lambda_\ell + \lambda_\ell^{-2}\lambda_\ell^2 + \lambda_\ell^{-3}\lambda_\ell^3 + \cdots + \lambda_\ell^{-N}\lambda_\ell^N = N.$$

This result could also be obtained directly, by considering the arrays

$$\tilde{X}_\lambda = (x_1, x_2, \cdots, x_N)_\lambda$$

in the N -dimensional coordinate space. This array is an eigenarray of the translation operator \hat{T} if

$$\hat{T}\tilde{X}_\lambda = \hat{T}(x_1, x_2, \cdots, x_N)_\lambda = \lambda(x_1, x_2, \cdots, x_N)_\lambda.$$

on the other hand

$$\hat{T}(x_1, x_2, \cdots, x_N)_\lambda = (x_2, x_3, \cdots, x_1)_\lambda,$$

hence, $x_j = \lambda x_{j-1}$ yielding $x_j = x_0 \lambda^j$, or $\tilde{X}_\lambda = x_0 (\lambda, \lambda^2, \cdots, \lambda^N)$.

Using the equations of motion, (15) (where we set $\ell = 0$), we obtain

$$\begin{aligned} \frac{d^2}{dt^2}\tilde{X}_\lambda &= \frac{d^2 x_0}{dt^2} (\lambda, \lambda^2, \cdots, \lambda^N) \\ &= \omega^2(x_{N-1} + x_1 - 2x_0) (\lambda, \lambda^2, \cdots, \lambda^N) \\ &= \omega^2 x_0 (\lambda^{N-1} + \lambda - 2) (\lambda, \lambda^2, \cdots, \lambda^N) \\ &= -\Omega_\lambda^2 \tilde{X}_\lambda. \end{aligned}$$

It follows that

$$\tilde{X}_\lambda(t) = \exp(\pm i\Omega_\lambda t)\tilde{X}_\lambda(0),$$

which can be written in the form

$$x_\ell = x_0 \lambda^\ell \exp(\pm i \Omega_\lambda t) = x_0 \exp\left(i \frac{2\pi}{L} a n \pm i \Omega_\lambda t\right).$$

7.11 Comparison of the normal mode and the atomic displacement pictures

Some final comments about the two pictures are made.

The classical version of the atomic displacement picture is equivalent to the “ansatz” that we wished to avoid. It provides the clearest description of the behavior of the atoms on the lattice, in the different normal modes. The normal coordinate picture provides the set of collective coordinates, in terms of which the (harmonic) Hamiltonian is separable: Expressing the Hamiltonian in terms of these normal coordinates, it becomes a sum of independent harmonic oscillators. The corresponding eigenfunctions are products of harmonic oscillator wave functions, each depending on one of the normal mode coordinates.

Both the atomic displacements picture and the normal mode picture allow quantum mechanical “algebraic” treatments, in which a set of independent creation-annihilation pairs is derived. These algebraic treatments are presented in the supplementary reading section, below.

8. Supplementary reading: Phonons as elementary excitations

In order to emphasize that learning is not terminated at the end of a semester, the present section is offered as “summer reading”. It provides an explicit explanation of the equivalence between the classical and the quantum mechanical derivations of the normal modes of a harmonic many-body system.

8.1 Review of the algebraic treatment of the harmonic oscillator

The Hamiltonian of the one-dimensional harmonic oscillator

$$\mathcal{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2} \hat{x}^2$$

can be written in the form

$$\mathcal{H} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right),$$

where

$$\begin{aligned} \hat{a} &= \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \frac{1}{\sqrt{2m\hbar\omega}} \hat{p} \\ \hat{a}^\dagger &= \sqrt{\frac{m\omega}{2\hbar}} \hat{x} - i \frac{1}{\sqrt{2m\hbar\omega}} \hat{p}. \end{aligned}$$

One easily verifies that $[\hat{a}, \hat{a}^\dagger] = 1$ and

$$[\mathcal{H}, \hat{a}^\dagger] = \hbar\omega\hat{a}^\dagger. \quad (23)$$

It follows that if ψ is an eigenfunction of \mathcal{H} with the eigenvalue E then

$$\begin{aligned} \mathcal{H}(\hat{a}^\dagger\psi) &= (\hat{a}^\dagger\mathcal{H} + \hbar\omega\hat{a}^\dagger)\psi \\ &= (E + \hbar\omega)(\hat{a}^\dagger\psi). \end{aligned}$$

Hence, $\hat{a}^\dagger\psi$ is an eigenfunction of \mathcal{H} with the eigenvalue $E + \hbar\omega$. This property means that \hat{a}^\dagger acts as a step-up operator from an eigenfunction of the harmonic oscillator to the eigenfunction with the next highest energy. Similarly, \hat{a} acts on any eigenfunction of the Hamiltonian as a step-down operator.¹⁹

It will be useful below to note that

$$[\mathcal{H}, \hat{x}] = \frac{\hbar}{im}\hat{p}, \quad (24)$$

and

$$[\mathcal{H}, \hat{p}] = im\omega^2\hbar\hat{x}.$$

8.2: Normal modes as “elementary excitations”

The algebraic representation of the harmonic oscillator reviewed above, that you are (most likely) familiar with from your basic quantum mechanics or quantum chemistry course, has an obvious but far reaching generalization. For an arbitrary Hamiltonian, \mathcal{H} , if we can find an operator, that we shall denote by \hat{A}^\dagger , that satisfies

$$[\mathcal{H}, \hat{A}^\dagger] = \lambda\hat{A}^\dagger \quad (25)$$

then the action of \hat{A}^\dagger on an eigenfunction of \mathcal{H} with an eigenvalue E produces an eigenfunction of \mathcal{H} with the eigenvalue $E + \lambda$. Equation (25) is sometimes satisfied only approximately, so \hat{A}^\dagger can be used (reasonably safely) to produce the first excited state from the ground state, even when climbing further up could be doubtful.

¹⁹To complete the discussion of the harmonic oscillator in terms of the step-up and step-down operators (sometimes called the creation and annihilation operators) we need to show that $\hat{a}\psi_0(x) = 0$, where $\psi_0(x)$ is the ground-state eigenfunction. Using the explicit form of \hat{a} this relation yields

$$\psi_0(x) = N_0 \exp\left(-\frac{m\omega}{2\hbar}x^2\right),$$

where N_0 has to be determined by normalization. It now follows that

$$\psi_1(x) = \hat{a}^\dagger\psi_0(x) = N_1x \exp\left(-\frac{m\omega}{2\hbar}x^2\right),$$

etc.

As a first application to the determination of the normal modes we consider the one-dimensional triatomic harmonic Hamiltonian introduced in section 7.4, *i. e.*,

$$\mathcal{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial x_3^2} \right) + \frac{k}{2} \left((x_2 - x_1)^2 + (x_3 - x_2)^2 \right). \quad (26)$$

Inspired by the treatment of the one-dimensional harmonic oscillator by means of the step-up and step-down operators \hat{a}^\dagger and \hat{a} , respectively, we attempt to construct analogous operators that will be relevant to our triatomic system. We start by considering the commutators

$$\begin{aligned} [\mathcal{H}, \hat{p}_1] &= i\hbar m \omega^2 (\hat{x}_1 - \hat{x}_2) \\ [\mathcal{H}, \hat{p}_2] &= i\hbar m \omega^2 (2\hat{x}_2 - \hat{x}_1 - \hat{x}_3) \\ [\mathcal{H}, \hat{p}_3] &= i\hbar m \omega^2 (\hat{x}_3 - \hat{x}_2) \end{aligned}$$

In complete analogy with the center-of-mass and the symmetric and antisymmetric coordinates (with respect to the permutation \hat{T}_{13}), discussed in section 7.4, we introduce

$$\begin{aligned} \hat{P} &= \frac{1}{3}(\hat{p}_1 + \hat{p}_2 + \hat{p}_3) \\ \hat{p}_a &= \hat{p}_3 - \hat{p}_1 \\ \hat{p}_s &= 2\hat{p}_2 - \hat{p}_1 - \hat{p}_3. \end{aligned}$$

It follows that

$$\begin{aligned} [\mathcal{H}, \hat{P}] &= 0 \\ [\mathcal{H}, \hat{p}_a] &= i\hbar m \omega^2 (\hat{x}_3 - \hat{x}_1) = i\hbar m \omega^2 \hat{x}_a \\ [\mathcal{H}, \hat{p}_s] &= i\hbar m \omega^2 3(\hat{x}_2 - \hat{x}_1 - \hat{x}_3) = i\hbar m \omega^2 3\hat{x}_s \end{aligned}$$

The first equation means that the center-of-mass momentum is constant. Application of the operator $\hat{T}_{1,3}$ to the left hand side of the second equation shows that it is antisymmetric, so the right hand side must be antisymmetric as well. Similarly, both sides of the third equation are symmetric with respect to the operation of \hat{T}_{13} .

To construct the corresponding step-up and step-down operators we note that

$$\begin{aligned} [\mathcal{H}, \hat{x}_a] &= -i\frac{\hbar}{m}\hat{p}_a \\ [\mathcal{H}, \hat{x}_s] &= -i\frac{\hbar}{m}\hat{p}_s \end{aligned}$$

It is now straightforward to show, using the commutators of the Hamiltonian with \hat{x}_a and with \hat{p}_a , that

$$[\mathcal{H}, \alpha\hat{x}_a + \beta\hat{p}_a] = \hbar\Omega_a(\alpha\hat{x}_a + \beta\hat{p}_a), \quad (27)$$

where $\Omega_a = \omega$ and $\frac{\alpha}{\beta} = im\omega$. Equation (27) suggests that

$$\hat{a}_a^\dagger = \alpha\hat{x}_a + \beta\hat{p}_a$$

acts as a step-up operator, like \hat{a}^\dagger in equation (23). The part of the Hamiltonian (26) that depends on the normal coordinate \hat{x}_a should, therefore, be of the form

$$\hbar\Omega_a\hat{a}_a^\dagger\hat{a}_a = \hbar\Omega_a(\alpha\hat{x}_a + \beta\hat{p}_a)(\alpha^*\hat{x}_a + \beta^*\hat{p}_a).$$

This expression looks like the Hamiltonian of a harmonic oscillator with some mass M , which is determined by writing the coefficient of \hat{p}_a^2 on the right-hand side in the form $\frac{1}{2M}$, and with a force constant $K = M\Omega_a^2$ which is determined by writing the coefficient of \hat{x}_a^2 in the form $\frac{M\Omega_a^2}{2}$. We obtain $M = m$, $\alpha = \sqrt{\frac{m\omega}{2\hbar}}$, and $\beta = \frac{i}{2m\hbar\omega}$. Hence,

$$\hat{a}_a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\hat{x}_a + \frac{i}{2m\hbar\omega}\hat{p}_a.$$

Exercise: Please write an expression for the frequency of the symmetric mode, and for the creation and annihilation operators that correspond to this mode.

8.3 The quantum mechanical treatment of a one-dimensional lattice within the normal-coordinate picture

We follow a straightforward generalization of the procedure illustrated in Section 8.1. We consider the Hamiltonian

$$\mathcal{H} = \sum_{j=1}^N \frac{\hat{p}_j^2}{2m} + \frac{k}{2} \sum_{j=1}^N (x_{j+1} - x_j)^2$$

and the operator

$$X_\lambda = c_0 \sum_{j=1}^N \lambda^{-j} x_j,$$

which is an eigenfunction of \hat{T} with the eigenvalue λ .

The commutator

$$[\mathcal{H}, X_\lambda] = \frac{\hbar}{im} c_0 \sum_{j=1}^N \lambda^{-j} \hat{p}_j = \frac{\hbar}{im} P_\lambda$$

suggests, by comparing with equation (24), that

$$P_\lambda = c_0 \sum_{j=1}^N \lambda^{-j} \hat{p}_j$$

is the momentum that corresponds to the coordinate X_λ (which is sometimes referred to as the momentum conjugate to X_λ).

Consistently, we obtain the commutator

$$[\mathcal{H}, P_\lambda] = \dots = \frac{k\hbar}{i} \left(\lambda + \frac{1}{\lambda} - 2 \right) X_\lambda = \frac{\hbar}{i} m\Omega_\lambda^2 X_\lambda,$$

where $\Omega_\lambda^2 = \omega^2 \left(\lambda + \frac{1}{\lambda} - 2 \right)$.

Defining

$$A_\lambda = \alpha X_\lambda + \beta P_\lambda$$

we find, using the commutation relations of the Hamiltonian with X_λ and with P_λ , that for an appropriate choice of $\frac{\alpha}{\beta}$ we have $[\mathcal{H}, A_\lambda] = -\hbar\Omega_\lambda A_\lambda$. When β is chosen appropriately then

$$\mathcal{H} = \sum_\lambda \hbar\Omega_\lambda A_\lambda^\dagger A_\lambda.$$

Hence, \mathcal{H} is a sum of N non-interacting harmonic oscillators, or normal modes. **Note that in this quantum mechanical treatment we do not need the classical equations of motion (Newton's second law) invoked above.**

The eigenvalues of \mathcal{H} are

$$E = \sum_\lambda \hbar\Omega_\lambda \left(n_\lambda + \frac{1}{2} \right),$$

and the eigenfunctions are

$$\Psi = \prod_\lambda \psi_\lambda(X_\lambda).$$

The time-dependent solutions are

$$\Psi(\{X_\lambda\}, t) = \prod_\lambda \psi_\lambda(X_\lambda) \exp\left(-i\frac{E}{\hbar}t\right).$$

8.4 More exotic quantum mechanical treatment: the atomic displacement picture

Once more, we consider the monoatomic one-dimensional lattice. The Hamiltonian is

$$\mathcal{H} = \sum_{j=1}^N \frac{\hat{p}_j^2}{2m} + \frac{k}{2} \sum_{j=1}^N (\hat{x}_{j+1} - \hat{x}_j)^2.$$

As before, we consider $\hat{X}_\lambda = (\hat{x}_1, \hat{x}_2, \dots, \hat{x}_N)_\lambda$ that satisfies $\hat{T}\hat{X}_\lambda = \lambda\hat{X}_\lambda$.

The Hamiltonian commutes with \hat{T} . Therefore, the commutator $[\mathcal{H}, \hat{X}_\lambda]$ satisfies

$$\hat{T}[\mathcal{H}, \hat{X}_\lambda] = \lambda[\mathcal{H}, \hat{X}_\lambda]$$

On the other hand

$$[\mathcal{H}, \hat{X}_\lambda] = \frac{\hbar}{im} (\hat{p}_1, \hat{p}_2, \dots, \hat{p}_N)_\lambda$$

yielding

$$\hat{T}(\hat{p}_1, \hat{p}_2, \dots, \hat{p}_N)_\lambda = \lambda(\hat{p}_1, \hat{p}_2, \dots, \hat{p}_N)_\lambda.$$

Hence, we define

$$\hat{P}_\lambda = (\hat{p}_1, \hat{p}_2, \dots, \hat{p}_N)_\lambda.$$

It is easy to verify that

$$[\mathcal{H}, \hat{P}_\lambda] = -\frac{\hbar k}{i} \hat{X}_\lambda,$$

suggesting that a ladder operator

$$\hat{A}_\lambda = \frac{1}{\sqrt{N}} (\alpha \hat{X}_\lambda + \beta \hat{P}_\lambda) = \frac{1}{\sqrt{N}} (\hat{a}_1, \hat{a}_2, \dots, \hat{a}_N)_\lambda$$

can be defined, where $\hat{a}_j = \alpha \hat{x}_j + \beta \hat{p}_j$ and $\hat{T}\hat{a}_j = \lambda \hat{a}_j$. This operator satisfies

$$[\mathcal{H}, \hat{A}_\lambda] = -\hbar\Omega_\lambda \hat{A}_\lambda.$$

The Hermitian conjugate of this relation is

$$[\mathcal{H}, \hat{A}_\lambda^\dagger] = \hbar\Omega_\lambda \hat{A}_\lambda^\dagger,$$

where

$$\hat{A}_\lambda^\dagger = \frac{1}{\sqrt{N}} \begin{pmatrix} \hat{a}_1^\dagger \\ \hat{a}_2^\dagger \\ \vdots \\ \hat{a}_N^\dagger \end{pmatrix}_{\lambda^*}.$$

It follows that

$$\begin{aligned}
[\hat{A}_\lambda, \hat{A}_{\lambda'}^\dagger] &= \frac{1}{N} \sum_{j=1}^N [\hat{a}_{\lambda,j}, \hat{a}_{\lambda',j}^\dagger] \\
&= \frac{1}{N} \sum_{j=1}^N [\lambda^j \hat{a}_0, (\lambda'^*)^j \hat{a}_0^\dagger] \\
&= \frac{1}{N} \sum_{j=1}^N \lambda^j (\lambda'^*)^j [\hat{a}_0, \hat{a}_0^\dagger] \\
&= \frac{1}{N} \sum_{j=1}^N (\lambda \lambda'^*)^j = \delta_{\lambda, \lambda'}.
\end{aligned}$$

The Hamiltonian can be written in the form

$$\mathcal{H} = \sum_{\lambda} \hbar \Omega_{\lambda} \left(\hat{A}_{\lambda}^{\dagger} \hat{A}_{\lambda} + \frac{1}{2} \right)$$

and the corresponding eigenvalues are

$$E = \sum_{\lambda} \hbar \Omega_{\lambda} \left(n_{\lambda} + \frac{1}{2} \right).$$

This quantum-mechanical atomic displacements picture does not seem to allow a coordinate-representation of the normal-mode wave functions of the kind introduced in footnote 19.

Exercise: Consider a one dimensional atomic lattice. Each atom has a mass M , the lattice parameter (distance between neighboring atoms) is a , and the (harmonic) force constant between neighboring atoms is K .

1. Please describe the normal mode with shortest wave length.
2. Please write an expression for the frequency of this normal mode.
3. Consider a normal mode with wave length $4a$, with a node between atom $j - 1$ and atom j : Please plot this wave and show how the atoms on the lattice oscillate.
4. Please calculate the frequency of this oscillation.
5. Now consider a mode with the same wave length ($4a$) but with a node on atom j : Please describe the oscillations of the atoms in this case.
6. Please calculate the frequency of this mode.
7. Please comment on these two distinct modes with equal wavelengths.
8. Please describe the vibrational mode with wave length $6a$, with a node on atom $j - 1$. What is its frequency?
9. Please describe the vibrational mode with wave length $6a$, with a node between atom $j - 1$ and atom j . What is its frequency?
10. The complete dispersion curve of vibrational frequencies of a one-dimensional lattice with one atom in each unit cell is given by the expression

$$\omega = 2\sqrt{\frac{K}{M}} \left| \sin \left(\frac{ka}{2} \right) \right|.$$

Please explain the connection of the frequencies calculated above to this expression.

You can find a solution of this exercise on the following page, but it will be more fun (and more rewarding) to try and solve it on your own.

Solution of the exercise: Consider a one dimensional atomic lattice. Each atom has a mass M , the lattice parameter (distance between neighboring atoms) is a , and the (harmonic) force constant between neighboring atoms is K .

1. Please describe the normal mode with shortest wave length.

The normal mode with the shortest wave length corresponds to an oscillation in which atom $j + 1$ moves to the left when atom j moves to the right. The wave length of this oscillation is $\lambda = 2a$.

2. Please write an expression for the frequency of this normal mode.

If atom j moves to the right by the amount x while both atoms $j - 1$ and $j + 1$ move to the left by the same amount, the force acting on atom j is $-4Kx$ so it satisfies the equation of motion

$$-4Kx = M \frac{d^2x}{dt^2} .$$

The frequency at which atom j (and all other atoms) oscillates is $\omega = \sqrt{\frac{4K}{M}} = 2\sqrt{\frac{K}{M}}$.

This problem can also be considered in the following way: All the even atoms oscillate together, forming a rigid body with mass $\frac{NM}{2}$, and all the odd atoms oscillate in the opposite direction, forming a rigid body of equal mass. The potential energy of the N atom chain is $N\frac{K}{2}(2x)^2 = \frac{NK}{2}(2x)^2$. Note that the relative coordinate is $2x$. The reduced mass of the two rigid bodies oscillating against one another is $\mu = \frac{NM}{4}$. The frequency of this mode is $\omega = \sqrt{\frac{NK}{\frac{NM}{4}}} = 2\sqrt{\frac{K}{M}}$.

3. Consider a normal mode with wave length $4a$, with a node between atom $j - 1$ and atom j : Please plot this wave and show how the atoms on the lattice oscillate.

Since there is a node between atom $j - 1$ and atom j , one wave length is completed by a node between atom $j + 3$ and atom $j + 4$. There is also a node at half wave length, between atom $j + 1$ and atom $j + 2$. When atom j moves to the right by x , then atom $j + 1$ moves to the right by the same amount, and atoms $j + 2$ and $j + 3$ move to the left by an equal amount.

4. Please calculate the frequency of this oscillation.

The force acting on atom j when it moves to the right is $-K(2x)$ because it is pulled by atom $j - 1$ but there is no force acting on it by atom $j + 1$. It follows that the frequency of its oscillation is $\omega = \sqrt{\frac{2K}{M}}$.

Here, just like in the previous case, half the atoms move (together, hence "rigidly") to the right while the other half move to the left. The total potential energy is

$$V = \frac{K}{2} \left((2x)^2 + (2x)^2 \right) \frac{N}{4} = \frac{KN}{4} (2x)^2 ,$$

because there are $\frac{N}{4}$ waves along a chain of length N , and within any four consecutive atoms (one wave length) there is one bond that decreases by $2x$ while another bond stretches by the same amount, and two bonds whose lengths remain a , the equilibrium

distance.

Since half the atoms move rigidly to the right while the other half move rigidly to the left, the reduced mass is $\mu = \frac{MN}{4}$, so the frequency is $\sqrt{\frac{2KN}{\frac{MN}{4}}} = 2\sqrt{\frac{2K}{M}}$.

5. Now consider a mode with the same wave length ($4a$) but with a node on atom j : Please describe the oscillations of the atoms in this case.

If there is a node on atom j , there is a node one wave length away, on atom $j + 4$. There must also be a node in between, on atom $j + 2$ (at half wave length). This means that $x_{j+3} = -x_{j+1}$.

6. Please calculate the frequency of this mode.

The atoms $j, j + 2, j + 4$, etc., are stationary. When the atom $j + 1$ moves to the right the force that acts on it is $-2kx$ because it is pulled by atom $j - 1$ and pushed by atom $j + 1$. Its frequency is $\omega = \sqrt{\frac{2K}{M}}$, just like the frequency of the oscillation described in section 3.

The other point of view starts from the fact that

$$V = \frac{K}{2}(4x^2) \left(\frac{N}{4}\right) = \frac{NK}{2}(2x)^2.$$

Note that the relative coordinate between the two moving subsystems is $2x$. Since $\frac{N}{4}$ atoms move to the right while $\frac{N}{4}$ atoms move to the left and $\frac{N}{2}$ atoms are stationary, it follows that the reduced mass is $\mu = \frac{NM}{8}$ and the frequency of this mode is

$$\omega = \sqrt{\frac{\frac{NK}{4}}{\frac{NM}{8}}} = \sqrt{\frac{2K}{M}}.$$

7. Please comment on these two distinct modes with equal wavelenghts.

The two modes described above have equal frequencies: they are degenerate. By taking linear combinations of these modes we can construct the mode in which the atoms $j + 1, j + 3$, etc. are stationary while the atoms $j, j + 4$, etc. move to the right when atoms $j + 2, j + 6$, etc., move to the left, or the mode in which there is a node between atom j and atom $j + 1$, then between atom $j + 2$ and atom $j + 3$, etc.

8. Please describe the vibrational mode with wave length $6a$, with a node on atom $j - 1$. What is its frequency?

One cycle of this wave is completed with a node on atom $j + 5$. There is a mid-wave node at atom $j + 2$. It follows that

$$x_j = x_{j+1} = -x_{j+3} = -x_{j+4}.$$

The force on atom j is $-Kx_j$ so its frequency is $\omega = \sqrt{\frac{K}{M}}$.

9. Please describe the vibrational mode with wave length $6a$, with a node between atom $j - 1$ and atom j . What is its frequency?

One cycle of this wave is completed with a node between atom $j + 5$ and atom $j + 6$. The mid-wave node is between atom $j + 2$ and atom $j + 3$. From the properties of the sin function it follows that

$$x_j = \frac{1}{2}x_{j+1} = x_{j+2} = -x_{j+3} = -\frac{1}{2}x_{j+4} = -x_{j+5}.$$

It follows that the force on atom j is

$$-k(x_j - x_{j-1}) + k(x_{j+1} - x_j) = -kx_j,$$

hence, the frequency of its vibration is $\omega = \sqrt{\frac{K}{M}}$.

10. The complete dispersion curve of vibrational frequencies of a one-dimensional lattice with one atom in each unit cell is given by the expression

$$\omega = 2\sqrt{KM} \left| \sin \left(\frac{ka}{2} \right) \right|.$$

Please explain the connection of the frequencies calculated above to this expression.

The frequency calculated in section 2 corresponds to $\lambda = 2a$ or $k = \frac{\pi}{a}$ (the boundary of the Brillouin zone). The frequencies calculated in sections 4 and 6 correspond to $\lambda = 4a$ or $k = \pm \frac{\pi}{2a}$ (recall that $\sin \left(\frac{\pi}{2} \right) = 1$ and $\sin \left(\frac{\pi}{4} \right) = \frac{\sqrt{2}}{2}$).

The frequency calculated in sections 7 and 8 corresponds to $k = \pm \frac{\pi}{3a}$ or $\frac{ka}{2} = \frac{\pi}{6}$, hence $\sin \left(\frac{ka}{2} \right) = \frac{1}{2}$.

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