

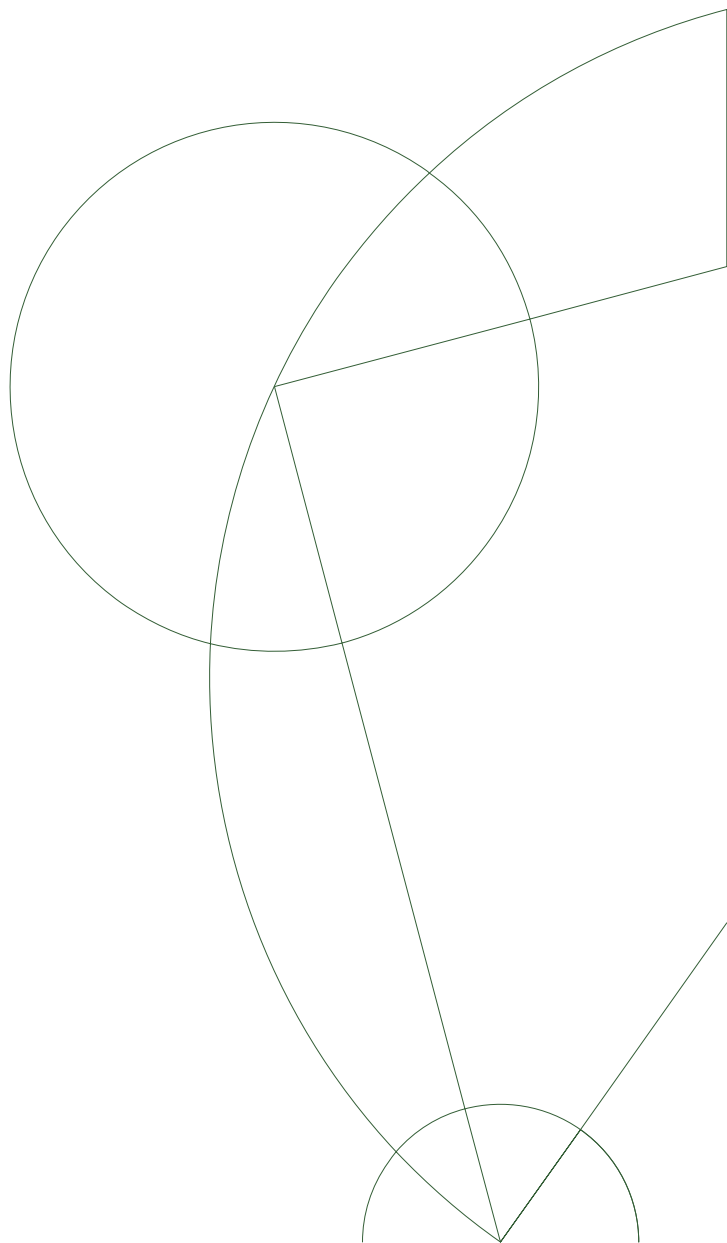


Master Thesis

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Ab initio Hartree-Fock for periodic helical systems Method development and applications to carbon nanotubes

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Abstrakt

Atom centreret ab initio Hartree-Fock introduceres for periodiske systemer med helisk symmetri. Et sådant system bliver konstrueret som et produkt af to krystal undergrupper, hvoraf den ene er cyklisk. Fock matrixen for et endelig gruppe af enhedsceller kan derved Fourier transformeres til en blok diagonal repræsentation. Disse sub-matricer diagonaliseres, og middelfeltet på den centrale enhedscelle udtrykkes efterfølgende i det direkte rum. Middelfeltet bliver dernæst pålagt alle celler ved tilføjelsen af Born-von Kármán periodiske grænsebetingelser. Dette itereres indtil selv-konsistens opnås, og densiteten derved spredes over nanorøret. Båndstrukturen konstrueres ved flere bånd diagrammer, en for hver af de ikke-reducerbare repræsentationer af den cykliske gruppe. Diagrammerne udregnes og analyseres for systemer af carbon nanorør med varierende helicitet og geometri, og det observeres at skaling af gitter vektoren inducerer en halvleder-metal faseovergang. Geometrisk optimering giver elastiske koefficienter, som bruges til at beskrive det radiale "breathing mode". Sammenligning med teoretiske modeller antyder at bånd-gabet overestimeres ved denne metode. Yderligere forbedringer præsenteres for at forklare elektron korrelation via MP2 og approksimeret Coupled Cluster.

nøgleord: Hartree Fock, atomistisk, helisk, nanorør, ab initio, båndstruktur, middelfelt, krystal grupper, blok diagonal, SCF

Abstract

Atom centred ab initio Hartree-Fock is introduced for periodic systems with helical symmetry. Such a structure is decomposed as a product of two crystal sub-groups, one of which being cyclic. This enables the Fock matrix of a finite cluster of cells to be Fourier transformed into a block diagonal form. The diagonalisation is performed on the sub-matrices and the mean field experienced by the central unit cell is expressed in the direct space. This environment is then imposed on all cells of the cluster by Born–von Kármán periodic boundary conditions. This is iterated until self consistency and then the density of the cluster is populated across the tube. The band structure arises in terms of multiple band diagrams, one for each irreducible representation of the cyclic group. Such diagrams are calculated and analysed for a system of carbon nanotubes, differing in both helicity and geometry. Scaling of the lattice vector is observed to result in a semiconducting-metallic phase transition. Geometry optimisation yields elastic coefficients that are used to describe the radial breathing mode. A comparison with theoretical models suggests that the obtained bandgaps are over-estimated. Further improvements are outlined to account for electron correlation by means of MP2 and approximated Coupled Cluster.

keywords: Hartree Fock, atomistic, helical, nanotubes, ab initio, band structure, mean field, crystal groups, block diagonal, SCF

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Nowadays it seems, that a moral conduct is hardly compatible with a worldly success. As the former calls for fairness in division, while the latter claims for oneself what many desire. In this regard I'm glad to know these three men; Jozef, Karsten and my dad. For they showed me such a simultaneous state can be lived, and that it begins with modesty, self discipline and effort to communicate. They have always made me feel that they believe in me, and I'm most grateful for that. There are many more whom I also wish to thank, particularly those who gave me chance, had patience with me or helped me along the way.

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Introduction

Arguably, the most straight-forward description of an arbitrary system starts with consideration of its energy. Since the energy is a scalar quantity, its enumeration is meaningless, unless there is at least one other value that it can be compared to. An obvious choice for this reference value is the energy corresponding to a state where all the constituents of the system are infinitely distant from one another. Then one can think of the total energy of the system as the difference between the reference “null” energy and energy of the assembled state. This assembled energy could encapsulates many kinds of contributions, all of which in general depend on positions or other attributes of one or multiple particles. This is reasonable as long as the magnitudes of such terms tend to zero at infinite separations. This is true for the two energy contributions considered in this work, namely the Coulomb and the Exchange. At infinite separation the Coulomb interaction vanishes because it is inversely proportional to the distance. The Exchange energy arises from the indistinguishability of particles at places where their densities overlap. However when infinitely apart, there is no overlap and therefore no ambiguity to which particle it is, and hence the Exchange energy is zero.

For a periodic system, however, the sum of all such contributions increases as more and more particles are considered. Therefore a macroscopic quantity should be defined as the total energy per one unit cell. In a crystalline system only two kinds of particles are considered, electrons and nucleons. Here it is appropriate to invoke the so called Born-Oppenheimer approximation. It assumes, and rightly so, that in the dynamical sense the motion of electrons and nucleons is completely decoupled. This is due fact that the mass of the electron is three orders of magnitude lighter than the nucleon’s and therefore also the processes between nuclei and respectively between electrons happen at different timescales. Much like the dynamics of a tennis ball bouncing off the ground is decoupled from the dynamics of the Earth orbiting the Sun. Naturally then, in approaching the problem one chooses a reference frame where the other behavior is traced out. Conventionally the positions of positive protons are considered first. For a chosen separation, one calculates the energy of assembling such a lattice of charges. Then the electrons, having the charge of the other kind, are let into the electric field created by the protons and relax in the most favorable states. Such states minimise the energy, and therefore not only must they be energy eigenstates, but also the ones with the smallest possible eigenvalue - the expectation value of the energy. Within Born-Oppenheimer approximation, there is not more to the electron-neutron interaction other than this. So the bottleneck of this approach is in calculating the most optimal states for the electrons to occupy for a given lattice potential. Naively speaking the electron prefers to be close to the proton, i.e. at the bottom of the potential well. Such a state is not unique and the vicinity of each of the protons would serve equally well. Unlike in the classical picture, where this degeneracy would break the translational symmetry by the particle settling in one of them, the quantum description allows for the particle to be tunneled into them all[1].

1 Fundaments of theory

Overveiw The electronic structure theory has been introduced by means of atomistic systems of increasing complexity. At first only single electron states were considered and the role of the symmetries and associated conserved quantities has been studied. The case of free particle demonstrates the conservation of linear momenta which is not present in bound states. For a particle in a spherically symmetric well the eigenstates were derived that form the spherical harmonics. This forms a complete basis set similar to the one used in the calculation. The double well problem gave rise to the concept of bonding and anti-bonding orbitals which was further developed in the context of periodic potential and Bloch functions. The elastic properties of bonds were addressed classically as validated by the Hellman-Feynman theorem which was also derived. The vibrational modes of the lattice were described as a continuation of the concept of elasticity. For the band structure to be obtained the method of Linear Combination of Atomic Orbitals was derived as a generalisation of Tight Binding model. This involved the concept of exchange degeneracy that resulted in the use of Slater determinants. Depending on the boundary conditions, the Hamiltonian matrix of LCAO is of the cyclic form and therefore some properties of representations of such groups were studied. At last the Hartree-Fock equations were derived that improve the single particle description by the presence of the mean field. For the scope of the project many electrons have to constitute this mean field. Therefore the Roothaan formulation of HF has been shown to turn the problem into the realm of linear algebra. This concludes the first section.

1.1 Continuous symmetry of free particle

A single particle is fully described by a quantum state $|\Psi\rangle$ that can be either pure, or if it cannot be described as such, it is referred to entangled. An entangled state correspond to a probabilistic mixture of several pure states, to which it can collapse by means of a measurement. Unlike the mixed state, that needs to be described as a probabilistic matrix, one can represent a pure state $|\Psi\rangle$ as a state vector. In what follows only pure states are considered. Such a state vector can be constructed in an arbitrary complete basis. One prefers a discrete basis to a continuous one, because then the whole problem can be recast into matrix quantum mechanics and can be addressed by means of linear algebra. In fact no physical phenomena is known to distinguish between distances of less than the Plank's length $l_p = \sqrt{\frac{\hbar G}{c^3}} \simeq 1.6 \cdot 10^{-35} m$. Therefore there is no need for a truly continuous basis, as the basis discretised by l_p would perform equally well. For practical reasons one wants to use as compact basis set as possible. The two most common representations of state vectors are the position and momentum representations. Each of them describes the state vector as a linear superposition of the elements that constitute its basis, either the discretised positions that a particle can take or discretised momenta that the particle can have. Thus one can construct the associated position or momentum wavefunction by projecting the state $|\Psi\rangle$ upon the chosen basis:

$$|\Psi\rangle = \left(\int_x |x\rangle \langle x| \right) |\Psi\rangle = \int_x |x\rangle \langle x | \Psi \rangle = \int_x |x\rangle \Psi(x) \cong \begin{pmatrix} \Psi(x)|_{x=x_1} \\ \Psi(x)|_{x=x_2} \\ \vdots \\ \Psi(x)|_{x=x_N} \end{pmatrix} \cdot \begin{pmatrix} |x_1\rangle \\ |x_2\rangle \\ \vdots \\ |x_N\rangle \end{pmatrix} = \mathbf{c}_i^{(x)} \cdot |\mathbf{x}_i\rangle \quad (1.1)$$

where the position wavefunction $\Psi(x) = \langle x | \Psi \rangle$ unfolds from the resolution of the identity. The scalar wavefunction $\Psi(x)$ represents the probability that the state will be found in the position described by the basis vector $|x\rangle$. Therefore one can construct from it the vector of coefficients $\mathbf{c}_i^{(x)}$, the norm squared of which equals unity. Likewise the state vector can be expressed in terms of momentum wavefunction $\Psi(p) = \langle p | \Psi \rangle$

$$|\Psi\rangle = \int_p |p\rangle \langle p | \Psi \rangle = \int_p |p\rangle \Psi(p) \cong \mathbf{c}_i^{(p)} \cdot |\mathbf{p}_i\rangle \quad (1.2)$$

One can express a stationary eigenstate of one representation in the other. For instance expressing an eigenstate of momentum p as an expansion in the x representation.

$$\langle x | p \rangle = \langle p | x \rangle^* = (2\pi\hbar)^{-\frac{1}{2}} e^{\frac{i}{\hbar} p \cdot x} = (2\pi)^{-\frac{1}{2}} e^{ik \cdot x} \quad (1.3)$$

where in the last term the expression for crystal momentum is introduced as $k = \hbar p$. Naturally it follows the corresponding wavefunctions are related by a Fourier transform because

$$\langle x | \psi \rangle = \sum_p \langle x | p \rangle \langle p | \psi \rangle = (2\pi\hbar)^{-\frac{1}{2}} \sum_p e^{\frac{i}{\hbar} p \cdot x} \psi(p) \quad (1.4)$$

A familiar application of the above is the description of a free particle, the hamiltonian of which reads

$$\hat{H} = \frac{\hat{p}}{2m} \quad (1.5)$$

Since the two representations $\{x\}, \{p\}$ are related by a Fourier transform one can express the momentum operator in the x representation as

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}. \quad (1.6)$$

There are no difficulties considering the external potential, since the particle is free and so its hamiltonian commutes with the momentum operator $[\hat{H}, \hat{p}] = 0$. So the momentum wavefunction is proportional to the derivative of the position wavefunction. So if a normalised wavepacket is localised to a small region of space the derivatives of its x wavefunction would span a bigger space than the derivatives of very delocalised one, which would be very close to zero. This means that the momentum of a particle has bigger freedom the more the position is constrained. This simply a manifestation of the Heisenberg's uncertainty principle

$$\sigma_x \cdot \sigma_p \geq \frac{\hbar}{2} \quad (1.7)$$

Noether's Theorem An effort was put on recovering as much as possible from Noether's theory for discrete symmetries. This is demonstrated by following few simple examples. A natural transition from a free particle to a particle in a spherical potential demonstrated how one loses the continuous translational symmetry and spacial boosts. This results in an absence of the general law of conservation of linear momenta, as the expectation value of the linear momenta of a single particle bound state is always zero. However still the angular momentum that arises as a Noether's charge[2] from the $SO(3)$ group remain true as the system is invariant under continuous rotation in three spacial coordinates. This is no longer true for the system of double well nor for a system of a crystal that is to be the centre of this study. The system of free particle is substantially different to the system of say a particle in a periodic potential and very little can be salvaged from Noether's theory for the case of the discrete symmetries[3].

1.2 Point symmetry and spherical harmonics

There are at least three good reasons why the system of a hydrogen is considered. Firstly, because it has a point symmetry that facilitates not only to the inversion but also to the continuous rotational symmetry. This gives rise to the conserved quantity of the angular momentum and also enables the separations of the three differential equations so that it is one of the very few quantum systems that can be solved analytically. Secondly the series of eigenstates that solve this system forms a complete basis set, the spherical harmonics, that is able to describe electrons in atomic systems in a very compact way, as opposed to the x or p basis sets. At last it is the most natural system to study, due to its abundance, and experimental feasibility. In fact it was this system that provided experimental grounds for the quantum theory.

The problem of relative motion of an electron and a nucleus can be solved by introducing an effective mass $\mu = \frac{mM}{m+M} \approx m$ in a Coulomb field $\frac{-Ze^2}{r}$. Then the stationary state of the electron, with eigenenergy E , is described by the wave function ψ , which solve the Schrodinger's equation

$$\left[\frac{\hbar^2}{2\mu} \Delta + E + \frac{Ze^2}{r} \right] \psi = 0. \quad (1.8)$$

Since the field in which the electron moves is centrally symmetric the system is invariant under continuous rotations in three spatial dimensions. The special orthogonal, $SO(3)$ group that constitute of all such rotations is mathematically equivalent, isomorphic, to the special unitary group $SU(2)$.

The particle in this eigenstate has therefore a definite magnitude of angular momentum which is conserved. One can therefore characterise each such state with two values only. One of the total angular momentum, squared for convenience, and a projection of this momentum to one of the axes, conventionally a spacial axis z .

$$\hat{l}^2 \psi = l(l+1) \psi \quad (1.9)$$

$$\hat{l}_z \psi = m \psi \quad (1.10)$$

$$\left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \theta^2} \right) \right] + l(l+1)\psi = 0 \quad (1.11)$$

$$i \frac{\partial \psi}{\partial \theta} + m\psi = 0 \quad (1.12)$$

rewriting in spherical coordinates

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) - \frac{l(l+1)}{r^2} \psi + \frac{2\mu}{\hbar^2} \left[E + \frac{Ze^2}{r} \right] \psi = 0^* \quad (1.13)$$

The the eigenstate must per se inherit the SO(3) invariance from the Hamiltonian and therefore it has to be decomposable into the product of independent radial $R(r)$ and spherical $Y_{lm}(\theta, \phi)$ components. The hilbert space is likewise formed of a tensor product of rotational and radial subspaces.

$$\psi = R(r) Y_{lm}(\theta, \phi). \quad (1.14)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{l(l+1)}{r^2} R + \frac{2\mu}{\hbar^2} \left[E + \frac{Ze^2}{r} \right] R = 0 \quad (1.15)$$

which gives rise to the asymptotic behavior as $r \rightarrow \infty$

$$\frac{d^2 R}{dr^2} + \frac{2\mu}{\hbar^2} E \cdot R = 0 \quad (1.16)$$

by integration of * the discrete energy eigenvalues can be obtained

$$E = -\frac{1}{2} \frac{Z^2}{n^2} \frac{\mu e^4}{\hbar^2}. \quad (1.17)$$

These values are historically provided the most crucial proof that validated the Schrodineger equation by means of experimental comparison to the atomic spectra of hydrogen.

For a given discrete radial spectrum $R_{nl}(r)$ the angular functions $Y_{lm}(\theta, \phi)$ can be determined so can the wavefunction associated with that state

$$\psi_{nlm} = R_{nl}(r) Y_{lm}(\theta, \phi). \quad (1.18)$$

The angular functions can be expressed in terms of the associated Legendre polynomials

$$P_l^m(\cos \theta) = \sin^{m\theta} \frac{d^m P_l(\cos \theta)}{(d \cos \theta)^m} \quad (1.19)$$

$$P_l(\cos \theta) = \frac{1}{2^l l!} \frac{d^l}{(d \cos \theta)^l} (\cos^2 \theta - 1)^l \quad (1.20)$$

in fact

$$Y_{lm}(\theta, \phi) = c P_l^m(\cos \theta) e^{im\phi} \quad (1.21)$$

where the constant is determined from the normalisation condition

$$\int_0^{2\pi} \int_0^\pi |Y_{lm}(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1 \quad (1.22)$$

those give rise to the hydrogen orbitals as we know them[4]. The spectrum of the spherical part constitutes of the spacial functions such as s, p,d, and the radial part scales the wavefunction as when the orbitals of higher order appear as in the wavefunction of e.g. $\psi_{1S}(\mathbf{r}) = \langle r | \varphi \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-\rho_1}$

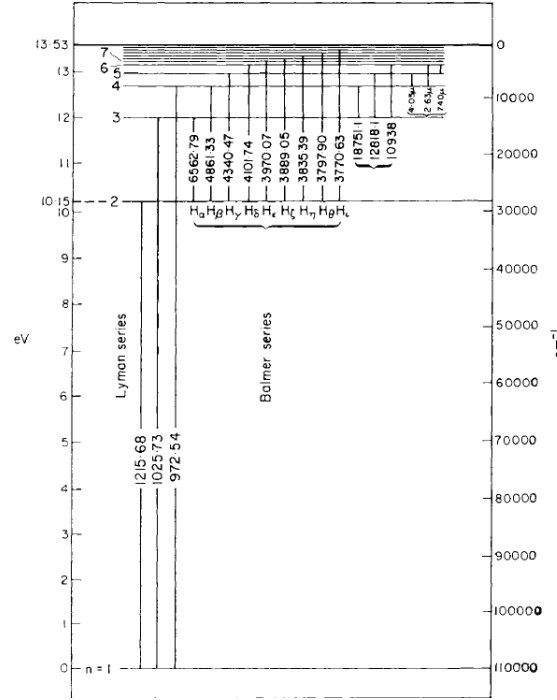


Figure 1.1: Electronic transition between the energy eigenstates can be compared to the frequencies of the spectral lines of the hydrogen gas. This constituted one of the main pieces of evidence of the quantum theory. Figure adapted from Sobel'man et al. [5]

1.3 Dihedral symmetry of H_2^+

To extend the description further one should consider the behavior of a single particle in a more complex potential. Particularly interesting is a potential that is symmetric under an inversion. This is because it provides valuable insights about the parity operation. The most natural system that demonstrates this is one of the $\mathbf{H}_2^+$ dimer. Not only it is convenient for experimental verifications but also serves as a building block for larger molecules, and ultimately for a bulk of a crystal also. The first assumption of the following analysis is the Born-Oppenheimer approximation[] that decouples the atomic and orbital motions because they happen at substantially different energy scales.

$$\left[\frac{\hbar^2}{2\mu} \Delta + E + \frac{e^2}{r_1} + \frac{e^2}{r_2} - \frac{e^2}{R} \right] \psi = 0. \quad (1.23)$$

When separation large, hamiltonian similar to hydrogen and so the orbitals.

$$\langle r | \varphi_1 \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-\rho_1} \quad (1.24)$$

$$\langle r | \varphi_2 \rangle = \frac{1}{\sqrt{\pi a_0^3}} e^{-\rho_2} \quad (1.25)$$

The trail kets are in general of the form

$$|\psi\rangle = c_1 |\varphi_1\rangle + c_2 |\varphi_2\rangle \quad (1.26)$$

The variational method consists of finding the stationary values of the

$$\langle H \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \epsilon[\psi] \quad (1.27)$$

where the second equality states that the energy is the functional of the wavefunction. This stems from analysis done Lanczos which states that any physical law which can be expressed as a variational principle describes a Self-adjoint operator. Which of course is true aforementioned quantum hamiltonian. The resolution of this eigenvalue problem within the subspace span by the linear combination of the two eigenkets $|\varphi_1\rangle, |\varphi_2\rangle$ is not straightforward as the two basis elements are not orthogonal. For an arbitrary vector $|\psi\rangle$ to be an eigenvector of the hamiltonian with the eigenvalue E it necessary and sufficient that:

$$\langle \varphi_i | H | \psi \rangle = E | \psi \rangle; \quad i = 1, 2 \quad (1.28)$$

that is:

$$\sum_{j=1}^2 c_j \langle \varphi_i | H | \varphi_j \rangle = E \sum_{j=1}^2 c_j \langle \varphi_i | \varphi_j \rangle \quad (1.29)$$

in order to construct the equations the elements of the overlap matrix S and hamiltonian H are defined as follows

$$S_{ij} = \langle \varphi_i | S | \varphi_j \rangle = \langle \varphi_i | \varphi_j \rangle \quad (1.30)$$

$$H_{ij} = \langle \varphi_i | H | \varphi_j \rangle \quad (1.31)$$

now the system of two linear homogeneous equations must be solved

$$(H_{11} - ES_{11}) c_1 + (H_{12} - ES_{12}) c_2 = 0 \quad (1.32)$$

$$(H_{21} - ES_{21}) c_1 + (H_{22} - ES_{22}) c_2 = 0 \quad (1.33)$$

which has a nonzero solution if and only if

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \quad (1.34)$$

for normalised basis elements the diagonal elements of the overlap matrix are equal unity $S_{ii} = 1$ and since the reference kets $|\varphi_1\rangle, |\varphi_2\rangle \in \mathfrak{R}$ the cross terms are equal

$$S_{ij} = S_{ji} = \langle \varphi_i | \varphi_j \rangle = \int d^3r \varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) \quad (1.35)$$

The elements of the Hamiltonian must obey the inversion symmetry since of the system so $H_{11} = H_{22}$ and also due to the realness of $|\varphi_1\rangle, |\varphi_2\rangle$ the cross elements must equal $H_{12} = H_{21}$.

$$H_{11} = \langle \varphi_1 | \left[\frac{\mathbf{P}^2}{2m} - \frac{e^2}{r_1} \right] | \varphi_1 \rangle - \langle \varphi_1 | \frac{e^2}{r_2} | \varphi_1 \rangle + \frac{e^2}{R} \langle \varphi_1 | \varphi_1 \rangle \quad (1.36)$$

$$H_{12} = \langle \varphi_1 | \left[\frac{\mathbf{P}^2}{2m} - \frac{e^2}{r_2} \right] | \varphi_2 \rangle - \langle \varphi_1 | \frac{e^2}{r_1} | \varphi_2 \rangle + \frac{e^2}{R} \langle \varphi_1 | \varphi_2 \rangle \quad (1.37)$$

the Coulomb integral

$$C = \langle \varphi_1 | \frac{e^2}{r_2} | \varphi_1 \rangle = \int d^3r \frac{e^2}{r_2} [\varphi_1(\mathbf{r})]^2 \quad (1.38)$$

the off diagonal integrals, also known as the resonance integrals, that enumerate the description of the instanton excitation resonating between the two wells.

$$A = \langle \varphi_1 | \frac{e^2}{r_1} | \varphi_2 \rangle = \int d^3r \varphi_1(\mathbf{r}) \frac{e^2}{r_1} \varphi_2(\mathbf{r}) \quad (1.39)$$

The the ground state solution is obtained by solving the determinant equation. Since this leads to a quadratic equation there exist two distinct solutions. Those are commonly referred to as bonding and antibonding solutions.

$$|\psi_+\rangle = \frac{1}{\sqrt{2(1-S)}} [|\varphi_1\rangle - |\varphi_2\rangle] \quad (1.40)$$

$$|\psi_-\rangle = \frac{1}{\sqrt{2(1+S)}} [|\varphi_1\rangle + |\varphi_2\rangle] \quad (1.41)$$

Those manifest the overall parity, given the reflection symmetry of the system, allowing the resulting state to be either symmetric or antisymmetric under the exchange of particles.

Note that in practice the matrix is diagonalised first. By the virtue of spectral theorem one can always find a basis that diagonalises a hermitian operator. Then the determinant of the diagonal matrix is simply

$$\det(\mathbf{D}) = \prod_{i=1}^n D_{ii} \quad (1.42)$$

1.4 Bonding, Antibonding, Elasticity

This analysis would also be valid for a discrete rotational invariance of a ring-like systems. Interestingly the boundary conditions would allow this to hold not only for infinite ring but also for finite one. For such rings the number of modes would be finite as they would have to be constructed from a superposition of finite set of states. Like in the case of the H_2 dimer the electrons in a ring like structure could also occupy the generalisation of bonding and antibonding states among more centres. However the ring periodicity constraints the number of nodal intersections to be even.

Hellman-Feynman Theorem

In the case of H_2 the separation between the atoms can be varied and corresponding energy calculated. One notices, as the energy is traced by the separation, that for the antibonding orbital the curve is monotonic and has no minimum. Therefore no stable bound state can be established. For the bonding orbital, however, such state exists and the single electron constitutes the chemical bond. This is experimentally observed as Lenard-Jones potential.

The hamiltonian of this dimer is a hermitian operator that is explicitly dependent on a real parameter i.e. separation of the hydrogen nuclei. Thus also the eigenstates and eigenvalues of this hamiltonian must alike depend on this parameter. What follows is the derivation of Hellman-Feynman theorem that states that the variation of the expectation value of a hermitian operator is proportional to the variation of its eigenvalue. It starts with the eigenvalue problem

$$H(R) |\psi(R)\rangle = E(R) |\psi(R)\rangle \quad (1.43)$$

then differentiate according to Leibniz rule

$$\frac{d}{dR} E(R) = \langle \psi(R) | \frac{d}{dR} H(R) | \psi(R) \rangle + \left\{ \left[\frac{d}{dR} \langle \psi(R) | \right] H(R) | \psi(R) \rangle + \langle \psi(R) | H(R) \left[\frac{d}{dR} | \psi(R) \rangle \right] \right\} \quad (1.44)$$

the claim of the theorem is that the rate of change of the eigenvalue with respect to a parameter of the hamiltonian reduces to only the first term of the expression above. This becomes obvious when one lets $H(R)$ act on the latter two terms in curly brackets, from left and right respectively. The two terms combined turn out to be just the derivative of scalar product of normalised eigenstate which has to be zero

$$E(R) \left\{ \left[\frac{d}{dR} \langle \psi(R) | \right] | \psi(R) \rangle + \langle \psi(R) | \left[\frac{d}{dR} | \psi(R) \rangle \right] \right\} = E(R) \frac{d}{dR} \langle \psi(R) | \psi(R) \rangle = 0 \quad (1.45)$$

$$1 = \langle \psi(R) | \psi(R) \rangle \quad (1.46)$$

Thus the equation reduces to

$$\frac{d}{dR} E(R) = \langle \psi(R) | \frac{d}{dR} H(R) | \psi(R) \rangle \quad (1.47)$$

This is a key result for the elastic properties as relates the variation of the expectation value of the hamiltonian, and relates it to the variation of the eigenvalue with respect to the same variable, as for instance the displacement from equilibrium. This provides the rationale for calculating the potential surfaces and identifying the elastic terms in the hamiltonian purely by studying of it eigenvalue changes in that parameter.

1.5 Phonons

Not only it is of common knowledge that a system tends towards an energetic minimum, but also that it oscillates in the vicinity of it. On the general grounds, this is due to the opposition of inertia and the potential field. In the case of inter-atomic oscillation the inertia stems from the kinetic energy and as usual acts against the change of system's momentum. One can think of the restoring force F_r , towards the equilibrium $a = a_0$, as arising to oppose a single parameter elastic field $V(a)$, that can be expanded as a polynomial in the displacement $|a - a_0|$ from the equilibrium lattice vector a_0

$$V(a) \simeq V(a_0) + V'(a_0)|a - a_0| + \frac{V''(a_0)}{2}|a - a_0|^2 + O(|a - a_0|^3) \quad (1.48)$$

In order to establish the equilibrium the force needs to integrate up to the magnitude of the field but be opposite in direction.

$$V(a) = - \int da F_r(a) = \int da m \frac{d^2 a}{dt^2} \quad (1.49)$$

or the gradient of the field must be equal to the force.

$$\nabla_a V(a) = -F_r(a) = m \frac{d^2 a}{dt^2} \quad (1.50)$$

This differential equation couples the behavior in a time domain to the behavior in domain of space by means of $a(t)$ which is function of both. To decouple this, one can decompose the function $a(t)$ in a linear superposition of simple oscillatory functions in time t ; $e^{-i\omega t}$. By the virtue of Fourier transform, the mixing coefficients $\tilde{a}(\omega)$ are no longer explicit functions of time, but functions of the corresponding frequencies ω only. Therefore their time derivative vanishes which facilitates the solution to the differential equation. Up to the normalisation of $\frac{1}{2\pi}$, which will cancel out, one expresses the Fourier transform of $a(t)$ simply as

$$a(t) = \int d\omega \tilde{a}(\omega) \cdot e^{-i\omega t} \quad (1.51)$$

and so the derivatives as

$$a(t)^{(N)} = \int d\omega (-i\omega)^N \tilde{a}(\omega) \cdot e^{-i\omega t} \quad (1.52)$$

To demonstrate this in practice, consider a simplified version of the field $V(a)$ expanded only to the second order. For small deviations, one would expect the linear term to vanish, because the neighborhood of the equilibrium is symmetric. If however the expansion is centered about

a point which lies outside of the equilibrium, which in this case it is not, the linear term would survive.

$$V(a) = V(a_0) + V'(a_0)|a - a_0| + \frac{V''(a_0)}{2}|a - a_0|^2 \quad (1.53)$$

$$V'(a_0) + V''(a_0)|a - a_0| = \nabla_a V(a) = -F_r(a) = m \frac{d^2 a}{dt^2} \quad (1.54)$$

Here it can be noted that since $a - a_0$ and a are related by only a translation in space, their derivatives are equal.

$$\frac{d^2 a}{dt^2} = \frac{d^2(a - a_0)}{dt^2} \quad (1.55)$$

$$M \frac{d^2(a - a_0)}{dt^2} = V'(a_0) + V''(a_0)|a - a_0| \quad (1.56)$$

Now one can evaluate the values of the gradients at a_0 . Naturally $V'(a_0)$ is zero and the second order gradient can be thought of as a stiffness of a hookean system $V''(a_0) \equiv K$. Also the origin on the coordinate system can be assumed far from the equilibrium, therefore $a \gg (a - a_0)$ and hence the absolute value can be dropped. For convenience the relabeling is introduced $x = a(t) - a_0$. The differential equation is thus reduced to

$$\frac{d^2 x(t)}{dt^2} = \frac{V''(a_0)}{m} x = \frac{K}{m} x(t) \quad (1.57)$$

A trained eye recognises that $x(t)$ must be a periodic function in t . Instead of solving this by means of such an ansatz, more general approach using Fourier transform is here employed.

$$x(t) = \int \frac{d\omega}{2\pi} \tilde{x}(\omega) \cdot e^{-i\omega t} \quad (1.58)$$

the equation can be recast

$$\int \frac{d\omega}{2\pi} \frac{d^2(\tilde{x}(\omega) \cdot e^{-i\omega t})}{dt^2} = \int \frac{d\omega}{2\pi} (-i\omega)^2 (\tilde{x}(\omega) \cdot e^{-i\omega t}) = \int \frac{d\omega}{2\pi} \frac{K}{m} \tilde{x}(\omega) \cdot e^{-i\omega t} \quad (1.59)$$

and now as long as the equality holds the integrands must be equal for each ω . Therefore $\forall \omega$ the integrals can be dropped and constants can be divided over.

$$(-i\omega)^2 \tilde{x}(\omega) \cdot e^{-i\omega t} = \frac{K}{m} \tilde{x}(\omega) \cdot e^{-i\omega t} \quad (1.60)$$

therefore only the frequencies that satisfy

$$(-i\omega)^2 = \frac{K}{m} \quad (1.61)$$

survive in the spectral expansion. Unsurprisingly this lead to the two roots $\omega = \pm \sqrt{\frac{K}{m}}$.

Phonons in 1D

To account for the phenomena of a dispersion one needs to consider the collective modes of many particles. In one dimension the hamiltonian will be equal to the following sum, where u_j are the displacement vectors of the particle j .

$$H_{ph} = \sum_{j=1}^N \left(\frac{1}{2M} p_j^2 + \frac{1}{2} K (u_j - u_{j-1})^2 \right) \quad (1.62)$$

At the scales where $\hbar$ ceases to be negligible the quantum effect have an influence. Therefore the commutation relationships need to be imposed for the atoms of the crystal

$$[p_{j_1}, u_{j_2}] = \frac{\hbar}{i} \delta_{j_1, j_2} \quad (1.63)$$

This problem at the equilibrium has a translational symmetry and therefore it is more convenient to approach it in the reciprocal space. The first Brillouin zone constitutes of following points

$$FBZ = \left\{ -\frac{\pi}{a} + \Delta k, -\frac{\pi}{a} + 2\Delta k, \dots, -\frac{\pi}{a} + N\Delta k \right\} \quad (1.64)$$

$$\Delta k = \frac{2\pi}{L} = \frac{2\pi}{a} \frac{1}{N} \quad (1.65)$$

The corresponding conjugate variables are obtained by Fourier transform

$$\begin{aligned} p_j &\equiv \frac{1}{\sqrt{N}} \sum_{k \in FBZ} p_k e^{ikR_j^0} & u_j &\equiv \frac{1}{\sqrt{N}} \sum_{k \in FBZ} u_k e^{ikR_j^0} & \delta_{R_j^0, 0} &= \frac{1}{N} \sum_{k \in FBZ} e^{ikR_j^0} \\ p_k &\equiv \frac{1}{\sqrt{N}} \sum_{j=1}^N p_j e^{-ikR_j^0} & u_k &\equiv \frac{1}{\sqrt{N}} \sum_{j=1}^N u_j e^{-ikR_j^0} & \delta_{k, 0} &= \frac{1}{N} \sum_{j=1}^N e^{-ikR_j^0} \end{aligned} \quad (1.66)$$

and then substituted into 1.62 to obtain the following

$$H = \sum_k \left(\frac{1}{2M} p_k p_{-k} + \frac{1}{2} M \omega_k^2 u_k u_{-k} \right) \quad (1.67)$$

$$\omega_k = \sqrt{\frac{K}{M^2}} \left| \sin \left(\frac{ka}{2} \right) \right| \quad (1.68)$$

$$[p_{k_1}, u_{k_2}] = \frac{\hbar}{i} \delta_{k_1, -k_2} \quad (1.69)$$

One would like to quantise this field and to do so the canonical form is employed[6]

$$\begin{aligned} b_k &\equiv \frac{1}{\sqrt{2}} \left(\frac{u_k}{l_k} + i \frac{l_k p_k}{\hbar} \right) & u_k &\equiv l_k \frac{1}{\sqrt{2}} (b_{-k}^\dagger + b_k) & l_k &= \sqrt{\frac{\hbar}{M \omega_k}} \\ b_{-k}^\dagger &\equiv \frac{1}{\sqrt{2}} \left(\frac{u_k}{l_k} - i \frac{l_k p_k}{\hbar} \right) & p_k &\equiv \frac{\hbar}{l_k} \frac{i}{\sqrt{2}} (b_{-k}^\dagger + b_k) \end{aligned} \quad (1.70)$$

and the second quantised hamiltonian appears as

$$H_{ph} = \sum_k \hbar \omega_k \left(b_k^\dagger b_k + \frac{1}{2} \right) \quad (1.71)$$

with the commutation relationships

$$\left[b_{k_1}, b_{k_2}^\dagger \right] = \delta_{k_1, k_2} \quad (1.72)$$

If one would like to treat a system of two atoms per unit cell, such as graphene or a carbon nanotube, the hamiltonian is thus modified as

$$H_{ph} = \sum_{k\lambda} \hbar\omega_{k\lambda} \left(b_{k\lambda}^\dagger b_{k\lambda} + \frac{1}{2} \right) \quad (1.73)$$

and the second set of indexes appears in quantisation

$$\left[b_{k_1\lambda_1}, b_{k_2\lambda_2}^\dagger \right] = \delta_{k_1, k_2} \delta_{\lambda_1, \lambda_2} \quad (1.74)$$

One then obtains the linear dispersion.

$$\omega(\mathbf{k}) = \sqrt{\frac{BK^2}{m}} = vk \quad (1.75)$$

The last step is to consider the partition function and possible microstates and thence the average occupation numbers based on the Boltzman distribution.[7]

The correction to the internal energy could then be expressed as

$$E = E_0 + 3N \frac{\hbar\omega_E \exp(-\beta\hbar\omega_E)}{1 - \exp(-\beta\hbar\omega_E)} \quad (1.76)$$

.

Cyclic groups and LCAO

After having discussed that the elastic and vibrational properties it is important to address the way how those stem from the electronic properties of the crystal. Let's examine the simplest scenario; one electron confined in a periodic 1D potential. Now in addition to $\hat{H}_0$, the Hamiltonian also constitutes of the potential $V(x)$, periodic under discrete translation by a .

$$V(x) = V(x + a) \quad (1.77)$$

Let's define discrete translational operator in terms of its action on the particle's eigenstate in x representation $|x'\rangle = \int_x |x\rangle \langle x| \Psi\rangle$.

$$\hat{\tau}(l) |x'\rangle = |x' + l\rangle \quad (1.78)$$

the operator being unitary but obviously not hermitian

$$\hat{\tau}(l)^\dagger x' \hat{\tau}(l) = x' + l \quad (1.79)$$

in case $l = a$

$$\hat{\tau}(a)^\dagger x \hat{\tau}(a) = V(x + a) = V(x) \quad (1.80)$$

and so translation by multiple of a commutes with both constituents of the hamiltonian

$$[\hat{H}, \hat{\tau}(a)] = 0 \quad (1.81)$$

now consider the potential being infinite everywhere except in the vicinity of periodically distributed sites. This prevents tunneling processes and delocalised states. Thus, despite having an infinite discrete spectrum of possible states (as in a molecule or a quantum dot), the particle is completely localised to particular site. Such state of particle bound to n^{th} site is represented by $|n\rangle$ that has no overlap with other sites $\delta_{mn} = \langle m | n \rangle$.

The translation operator transforms state

$$\hat{\tau}(a) |n\rangle = |n+1\rangle \quad (1.82)$$

and therefore $|n\rangle$ is definitely not an eigenstate of $\hat{\tau}(a)$.

To try to find a simultaneous eigenstate of both $\hat{\tau}(a)$ and $\hat{H}$ we combine all those states

$$|\theta\rangle \equiv \sum_n e^{in\theta} |n\rangle \quad (1.83)$$

which indeed is an eigenstate for an infinite linear chain[8]

$$\hat{\tau}(a) |\theta\rangle = \hat{\tau}(a) \sum_n e^{in\theta} |n+1\rangle = \sum_{n=-\infty}^{\infty} e^{i(n-1)\theta} |n\rangle = e^{-i\theta} |\theta\rangle \quad (1.84)$$

if the periodic boundary conditions are applied the diagonal elements of single particle hamiltonian are identical due to the matrix being a cyclic one.

Groups and cyclic Matrices To tackle the problem of identifying many-body eigenvectors of a periodic system, first consider a chain of hydrogen atoms. The premise is that if the spacing would be sufficiently large the single electron wavefunctions of electrons would be localised to the atomic sites, having no overlap with the neighboring electrons. This would prevent any form of correlation between the electrons and every one would behave as in an isolated hydrogen atom. As the lattice spacing would gradually shrink at some point the hydrogens would pair up to form bound states of H_2 molecules with lower energy eigenvalue per electron. If however, by a theoretical construct, the equal spacing would be maintained, the problem can be analysed using group theory[9].

For simplicity let's introduce a cyclic boundary condition so that the group is formed of elements $A_1 = (A)$, $A_2 = (A)^2, \dots, E = (A)^h$ so that the translation operations form a cyclic group with h classes and therefore h irreducible representations.

$$\Gamma(A) = \begin{pmatrix} \Gamma^{(1)}(A) & & & 0 \\ & \Gamma^{(2)}(A) & & \\ & & \ddots & \\ 0 & & & \Gamma^{(h)}(A) \end{pmatrix} \quad (1.85)$$

Consider now a number representation of those group elements in which $\Gamma(A) = r$. Then

for this representation $\Gamma(A_n) = \Gamma(A)^n = r^n$ holds, in particular $\Gamma(E) = 1$ and therefore $\Gamma(E) = \Gamma(A)^h = r^h = 1$. Straightforward solution for r can be found in $\mathbb{C}^2$ as the h^{th} root of unity $r = e^{i2\pi p/h}$ where $p = 1, 2, \dots, h$. Those are all the h irreducible representations we were after $\Gamma^{(p)}(A) = e^{i2\pi p/h}$ with $p = 1, 2, \dots, h$.

The system of our interest possesses this cyclic symmetry and therefore its Hamiltonian must per se inherit it. In case of the hydrogen ring the group element A represents the displacement by the spacing a which can be thought of as a shift of the periodic potential by $-a$. One can think of this in terms of transformation operators P_A , associated with this symmetry group, such that $P_A\psi(x) = \psi(x + a)$. These operators commute with the Hamiltonian

$$\hat{P}_A \hat{H} \psi_n = \hat{P}_A E_n \psi_n \quad (1.86)$$

$$\hat{H}(\hat{P}_A \psi_n) = E_n(\hat{P}_A \psi_n) \quad (1.87)$$

so that any eigenfunction ψ_n transformed by symmetry operator $\hat{P}_A$ will also be an eigenfunction of the hamiltonian $\hat{H}$ with the same energy eigenvalue E_n . This implies that all the solution of the p^{th} representation ψ_p satisfy the following

$$\psi_p(x + a) = \hat{P}_A \psi_p(x) = \Gamma^{(p)}(A) \psi_p(x) = e^{i2\pi p/h} \psi_p(x) \quad (1.88)$$

with the boundary condition being that the circumference of the ring $L = ah$ where $\frac{a}{L} \ll 1$. By replacing the index of irreducible representations p with a new one k such that $k = \frac{2\pi p}{L} = \frac{2\pi p}{ah}$ one can recast the equality for the eigenfunction to be

$$\psi_p(x + a) = e^{i2\pi pa/L} \psi_p(x) = e^{ika} \psi_p(x) \quad (1.89)$$

and upon relabeling $\psi_p = \psi_k$ one obtains $\psi_k(x + a) = e^{ika} \psi_k(x)$. It follows that that any function ψ_k of this kind can be described as a product of a periodic function $u_k(x) = u_k(x + a)$ with a phase factor. These function for all of the discrete values of k are referred to as Bloch states[10].

$$\psi_k(x) = u_k(x) e^{ika} \quad (1.90)$$

As the periodic function $u_k(x)$ it is convenient to use the atomic orbital basis $|\rho^R\rangle$ localised at each atom with the period of the lattice spacing.

Periodic LCAO

The first crude approximation comes by assuming that the full crystal Hamiltonian can be, in the vicinity of the nucleus, described by that of a single atom H_{at} . It also follows the electronic states are well localised and are the eigenstates of H_{at}

$$H_{at} \psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r}) \quad (1.91)$$

$$= E_n \psi_n (\mathbf{r} - \mathbf{R}) \quad (1.92)$$

We shall also include the correction the the crystal Hamiltonian:

$$H = H_{at} + \Delta U (\mathbf{r}) \quad (1.93)$$

As shown argued above, the crystal Hamiltonian as well as the single electron wavefunction must exhibit the translational symmetry so the wavefunctions will preserve their form for all $\mathbf{R}$ in the Bravais lattice. In order for the Bloch description to be preserved, the suitable wavefunction must be formed as a linear combination of the wavefunction that satisfy the Bloch condition.

$$\psi_{n\mathbf{k}} = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \psi_n (\mathbf{r} - \mathbf{R}) \quad (1.94)$$

where $\mathbf{R}$ runs through the N values of the first Brillouin zone.

It can be verified that this wavefunction satisfies the Bloch condition as follows[11]:

let $\psi_{n\mathbf{k}} \rightarrow \psi$

$$\psi(\mathbf{r} + \mathbf{R}) = \sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot \mathbf{R}'} \psi_n (\mathbf{r} + \mathbf{R} - \mathbf{R}') \quad (1.95)$$

$$= e^{i\mathbf{k} \cdot \mathbf{R}} \left[\sum_{\mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R}' - \mathbf{R})} \psi_n (\mathbf{r} - (\mathbf{R}' - \mathbf{R})) \right] \quad (1.96)$$

$$\bar{\mathbf{R}} \equiv (\mathbf{R}' - \mathbf{R}) \quad (1.97)$$

$$= e^{i\mathbf{k} \cdot \mathbf{R}} \left[\sum e^{i\mathbf{k} \cdot \bar{\mathbf{R}}} \psi_n (\mathbf{r} - \bar{\mathbf{R}}) \right] \quad (1.98)$$

$$= e^{i\mathbf{k} \cdot \mathbf{R}} \psi (\mathbf{r}) \quad (1.99)$$

However this simplified description is built on the premise that the electronic states are precisely of the form of the atomic orbitals. To generalise this one has to allow the eigenstates $\phi(\mathbf{r})$ to differ from $\psi(\mathbf{r})$ and they should be determined by further calculation. Due to fact that ψ_n form a complete basis one can expand ϕ in a small number of ψ [10].

$$\phi(\mathbf{r}) = \sum_{\mathbf{R}} b_n \psi_n (\mathbf{r}) \quad (1.100)$$

Apply this result to the Schrödinger equation

$$H\psi(\mathbf{r}) = (H_{at} + \Delta U(\mathbf{r}))\psi(\mathbf{r}) = \epsilon(\mathbf{k})\psi(\mathbf{r}) \quad (1.101)$$

by multiplying it by the atomic orbitals $\psi_m^*(\mathbf{r})$ and integrating over all $\mathbf{r}$

$$\langle \psi_m | H_{at} | \psi \rangle = \langle H_{at} \psi_m | \psi \rangle = E_m \langle \psi_m | \psi \rangle \quad (1.102)$$

$$(\epsilon(\mathbf{k}) - E_m) \langle \psi_m | \psi \rangle = \langle \psi_m | \Delta U(\mathbf{r}) | \psi \rangle \quad (1.103)$$

since the atomic orbitals satisfy the orthonormality condition

$$\langle \psi_m | \psi_n \rangle = \delta_{mn} \quad (1.104)$$

we can thus determine the coefficients $b_n(\mathbf{k})$ [12]

$$\begin{aligned} (\epsilon(\mathbf{k}) - E_m) b_n(\mathbf{k}) = & \\ & - (\epsilon(\mathbf{k}) - E_m) \sum_n \left(\sum_{R \neq 0} \langle \psi_m | \psi_n(\mathbf{r} - \mathbf{R}) e^{ik \cdot R} \rangle \right) b_n \\ & + \sum_n \langle \psi_m | \Delta U(\mathbf{r}) | \psi_n \rangle b_n \\ & + \sum_n \left(\sum_{R \neq 0} \langle \psi_m | \Delta U(\mathbf{r}) | \psi_n(\mathbf{r} - \mathbf{R}) e^{ik \cdot R} \rangle \right) b_n \end{aligned} \quad (1.105)$$

where the first term on the RHS contains integrals that can be calculated numerically

$$\int d\mathbf{r} \psi_m * \psi_n(\mathbf{r} - \mathbf{R}) \quad (1.106)$$

Many particle Origin of exchange degeneracy

The concept of exchange degeneracy is commonly referred to in terms of the correction of the many body energy eigenvalue. It arises from the indistinguishability of quantum particles at point where the mutual overlap of their probability densities is non-zero. It needs to be understood that the concept of exchange degeneracy naturally arises from the invariance of the system under the exchange of any two particles. So it comes a priori to the parity consideration (i.e. either for fermionic or bosonic systems) and regardless of the interaction between the particles, or lack thereof. To see this clearly, consider an interactionless manybody system. the manybody hamiltonian $\hat{H}$ constitutes of merely the sum of one body hamiltonians $\hat{H}_1$ that act only on the space spanned by the corresponding particle described by $\mathbf{r}_i$.

$$\left[\hat{H}_1 + \hat{H}_2 + \cdots + \hat{H}_N \right] \psi(\mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_N) = E \psi(\mathbf{r}_1 + \mathbf{r}_2 + \cdots + \mathbf{r}_N) \quad (1.107)$$

This is a common eigenvalue problem that consists of finding a vector that is invariant under the transformation, up to a scaling constant which is its eigenvalue. The solutions of this are not unique, in fact the spectrum of suitable energy eigenvalues E_k and corresponding eigenvectors φ_k is as big as the number of basis elements, orbitals χ_k , used to describe the many body wavefunction. This is obvious as one essentially solves the problem of diagonalisation of the matrix $\hat{H} - E_k$ and so the number of eigenvalues (i.e. elements on the diagonal), is the same as the dimension of the matrix (i.e. the size of the basis). Then due to the lack of interaction this can be split into N separate equations [13]

$$\hat{H}_i(\mathbf{r}_i) \psi(\mathbf{r}_i) = E_k \varphi_k(\mathbf{r}_k) \quad (1.108)$$

$$i = 1, 2 \dots, N; k = 1, 2 \dots \quad (1.109)$$

The many body wavefunction is merely the tensor product of single body wavefunctions, whereas for now no other constraints are put on the particular choice of eigenfunctions for each particle.

$$\psi(\mathbf{r}_1 + \mathbf{r}_2 + \dots + \mathbf{r}_N) = \prod_{i=1}^N \varphi_k(\mathbf{r}_i) \quad (1.110)$$

There is an ambiguity in the above-described Hartree function created by the one electron orbitals. Generally speaking Hartree function only involves the product of $u_i(r_i)$ that commute $[u_i(r_i), u_j(r_j)] = 0 \forall i, j$ and therefore is invariant under permutation of them. This implies that also any linear combination of them would serve equally well.

$$\psi = \sum_p c_p \hat{P} [u_1(1) u_2(2) \dots u_N(N)] \quad (1.111)$$

where $\hat{P}$ permutes the order of the electrons and c_p is the weight associated with that permutation. Since the application of the same Permutation operator twice in succession restores the original state $P_{ik}^2 \psi = \psi$, it must hold that $P_{ik} \psi = (\pm 1) \psi$. In other words the wavefunction is allowed to belong only to either symmetric or antisymmetric one-dimensional representation of the permutation group. Experimental evidence confirms that electrons as well as other spin-half particles belong to the antisymmetric representation and therefore the Hartree function associated with a many particle state must be anti-symmetric in the exchange of any two of its constituent electrons.

$$\Psi = A\psi(r_1, \dots, r_N) = (N!)^{-\frac{1}{2}} \sum_P (-1)^p \hat{P} \psi(r_1, \dots, r_N) \quad (1.112)$$

Where A is defined to be the Antisymmetriser[14] operator, and p labels the binary permutation in the Permutation operator. One can easily be convinced that the anti-symmetriser product is equivalent to the determinant referred to as Slater determinant[15].

$$\Psi = (N!) \begin{vmatrix} u_1(1) & u_2(1) & & u_N(1) \\ u_1(2) & u_2(2) & & u_N(2) \\ & & \ddots & \\ u_1(N) & & & u_N(N) \end{vmatrix} \quad (1.113)$$

1.6 Hartree-Fock , Roothaan formalism

Firstly the concept of the mean field is introduced in an abstract theoretical manner. In this representation the particularities of the implementation, such as the basis set or the interaction potential, are not considered and the theory is treated on general grounds. However it needs to be understood that in order to perform numerical calculations of quantitative kind, the problem needs to be interpreted in terms of linear algebra. This is due to the fact that the symbolic computation,

i.e. solving equations by isolation of variables, is rendered ineffective compared to when matrix diagonalisation is applicable. Therefore eventually one needs to express the state functions as vectors in terms of a compact basis and the operators as matrices with elements representing how basis functions transform under that operation.

The Hamiltonian

$$H = \sum_i^N \left[\frac{\mathbf{p}_i^2}{2m} - \frac{Ze^2}{r_i} + \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i \right] + \sum_{i>j} \frac{e^2}{r_{ij}} \quad (1.114)$$

is too complicated on its own to be handled at once. It can therefore be thought of as spherically symmetric term H_0 which is perturbed by H' .

$$H_0 = \sum_i \left[\frac{\mathbf{p}_i^2}{2m} + U(r_i) \right] \quad (1.115)$$

$$H' = \sum_i \left[\sum_{j>i} \frac{e^2}{r_{ij}} - \frac{Ze^2}{r_i} - U(r_i) \right] + \sum_i \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i \quad (1.116)$$

The generalisation of single particle wavefunction to many particle wavefunction can be approached by assuming that the many particle function can be written as a product of single particle functions.

$$\psi(\mathbf{r}_1, s_1, \dots, \mathbf{r}_N, s_N) = u_1(\mathbf{r}_1) \chi(s_1) \dots u_N(\mathbf{r}_N) \chi(s_N) \quad (1.117)$$

This is a straightforward choice as the conditional probability distribution is recovered by multiplication of individual probability amplitudes. Clearly, this Hartree function cannot in principle account for correlation of particles as the the probability amplitude of one particle is independent of the instantaneous position of another.

The iterative procedure starts by initial guess of one electron orbital functions $u_i(r_i)$ then one calculates the spherically averaged potential perceived by one electron from the presence of the remaining electrons.

$$U_i(r_i) = \frac{-Ze^2}{r_i} + \left[\sum_{i \neq j} \frac{e^2}{r_{ij}} \right]_{av.} \quad (1.118)$$

This is followed by solving the Schrödinger equation by numerical integration equation for every electron i

$$\left[\frac{\mathbf{p}_i^2}{2m} + U_i(r_i) \right] u_i = E_i u_i \quad (1.119)$$

This is repeated until self-consistency. It can also be shown that the self consistency condition minimises the energy as in the variational theorem.

Mean field in 2nd quantisation

For completeness the method of Hartree-Fock is presented in the second quantisation. The derivation below is adapted from Bruus Flensberg [6].

The full hamiltonian can be described as the sum of the one body part and the mean field potential

$$H = H_0 + V_{int} \quad (1.120)$$

The canonical form of the second quantised single body hamiltonian has form

$$H_0 = \sum_i \epsilon_i c_i^\dagger c_i \quad (1.121)$$

and the two body interaction operator sums over two sets of indexes

$$V_{int} = \frac{1}{2} \sum_{ii',jj'} V_{ij,ij'} c_i^\dagger c_j^\dagger c_{j'} c_{i'} \quad (1.122)$$

the density operator is as usual

$$\rho_{ii'} = c_i^\dagger c_{i'} \quad (1.123)$$

is only large when the statistical average is $\langle \rho_{ii'} \rangle$ nonzero, which is quite seldom so. Therefore one can express the interaction operator in terms of a deviation from its average such that

$$c_i^\dagger \left(c_j^\dagger c_{j'} - \langle c_j^\dagger c_{j'} \rangle \right) c_{i'} + c_i^\dagger c_{i'} \left(c_j^\dagger c_{j'} - \langle c_j^\dagger c_{j'} \rangle \right) \quad (1.124)$$

$$\left(c_i^\dagger c_{i'} - \langle c_i^\dagger c_{i'} \rangle \right) \left(c_j^\dagger c_{j'} - \langle c_j^\dagger c_{j'} \rangle \right) + c_i^\dagger c_{i'} \langle c_j^\dagger c_{j'} \rangle + c_j^\dagger c_{j'} \langle c_i^\dagger c_{i'} \rangle - \langle c_i^\dagger c_{i'} \rangle \langle c_j^\dagger c_{j'} \rangle \quad (1.125)$$

this naturally separate the terms into the Coulomb and Exchange, also referred to as Hartree and Fock terms, the last term vanishes.

$$V_{int}^{hartree} = \frac{1}{2} \sum V_{ij,ij'} n_{jj'} c_i^\dagger c_{i'} + \frac{1}{2} \sum V_{ij,ij'} n_{ii'} c_j^\dagger c_{j'} - \frac{1}{2} \sum V_{ij,ij'} n_{ii'} n_{jj'} \quad (1.126)$$

$$V_{int}^{fock} = -\frac{1}{2} \sum V_{ij,ij'} n_{ij'} c_j^\dagger c_{i'} - \frac{1}{2} \sum V_{ij,ij'} n_{ji'} c_i^\dagger c_{j'} + \frac{1}{2} \sum V_{ij,ij'} n_{ij'} n_{ji'} \quad (1.127)$$

total hamiltonian

$$H^{HF} = H_0 + V_{int}^{hartree} + V_{int}^{fock} \quad (1.128)$$

now consider the above-mentioned case of electrons in a periodic one dimensional lattice. The convenient choice of basis is the bloch orbitals c_k , which are orthogonal, therefore also the

matrix of coefficients of expectation value $\langle c_k^\dagger c_{k'} \rangle$

$$H^{HF} = \sum \epsilon_{\mathbf{k}}^{HF} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} \quad (1.129)$$

then the final energy equals

$$\begin{aligned} \epsilon_{\mathbf{k}}^{HF} &= \epsilon_{\mathbf{k}} + \sum_{\mathbf{k}'\sigma'} [V(0) - \delta_{\sigma\sigma'} V(\mathbf{k} - \mathbf{k}')] n_{\mathbf{k}'\sigma} \\ &= \epsilon_{\mathbf{k}} + V(0) N - \sum_{\mathbf{k}'\sigma'} V(k - k') n_{\mathbf{k}'\sigma'} \end{aligned} \quad (1.130)$$

Roothaan equations

The above describes how to, for a given state, calculate the energy eigenvalue that includes the contributions of the many body Coulomb interactions by means of the mean field. However it is not guaranteed that the lowest eigenvalue corresponding to the eigenvectors is in fact the minimum for such a system. Since the interaction terms are themselves functions of the state vector it is impossible find the minimum in an analytic way, unless perhaps in exceptional cases where the system posses symmetry that would render the problem feasible. Since this is not in general the case for the iterative procedure is thus introduced.

Consider a state φ defined by coefficients in certain basis χ

$$\varphi_i = \sum_p \chi_p C_{pi} \quad (1.131)$$

where the χ_p 's are normalised orbitals

$$\int \bar{\chi}_p \chi_p dv = 1 \quad (1.132)$$

To turn the problem to one of the linear algebra the vector and matrix notation is introduced

$$\chi = \begin{pmatrix} \chi_1 & \chi_2 & \dots & \chi_m \end{pmatrix} \quad (1.133)$$

for the states

$$c_i = \begin{pmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{mi} \end{pmatrix} \quad (1.134)$$

for the coefficients. So we can express any state such as

$$\varphi_i = \chi c_i \quad (1.135)$$

$$\phi = \chi C \quad (1.136)$$

the one electron operators M and the matrix that collects all the elements are defined as

$$M_{pq} = \int \bar{\chi}_p M \chi_p dv \quad (1.137)$$

$$M = \begin{pmatrix} M_{11} & M_{12} & & \\ & & & \\ & & & \\ M_{m1} & M_{m2} & & M_{mm} \end{pmatrix} \quad (1.138)$$

if the basis is not orthogonal the overlap integral between the orbitals of the basis is defined

$$S_{pq} = \int \bar{\chi}_p \chi_q dv \quad (1.139)$$

The usefulness of this notation is manifested here as the integral is equivalent to the product of a matrix and vectors.

$$\int \varphi_i M \varphi_j dv = \mathbf{c}_i^* \mathbf{M} \mathbf{c}_j \quad (1.140)$$

for orthogonal basis

$$\int \varphi_i \varphi_j dv = \mathbf{c}_i^* \mathbf{S} \mathbf{c}_j = \delta_{ij} \quad (1.141)$$

$$H_i = \mathbf{c}_i^* \mathbf{H} \mathbf{c}_j \quad (1.142)$$

$$\delta H_i = (\delta \mathbf{c}_i^*) \mathbf{H} \mathbf{c}_j + \mathbf{c}_i^* \mathbf{H} (\delta \mathbf{c}_i) \quad (1.143)$$

the Coulomb operator J and exchange operator K are likewise defined

$$J_{ij} = \mathbf{c}_i^* \mathbf{J}_j \mathbf{c}_i = \mathbf{c}_j^* \mathbf{J}_i \mathbf{c}_j \quad (1.144)$$

$$K_{ij} = \mathbf{c}_i^* \mathbf{K}_j \mathbf{c}_i = \mathbf{c}_j^* \mathbf{K}_i \mathbf{c}_j \quad (1.145)$$

introduce variational concept by varying $\mathbf{c}_i$ as $\delta \mathbf{c}_i$. The corresponding variation in energy is

$$\delta E = 2 \sum_i \delta H_i + \sum_{ij} (2\delta J_{ij} - \delta K_{ij}) \quad (1.146)$$

$$= 2 \sum_i [(\delta \mathbf{c}_i^*) \mathbf{H} \mathbf{c}_j + \mathbf{c}_i^* \mathbf{H} (\delta \mathbf{c}_i)] \quad (1.147)$$

$$+ \sum_{ij} [\delta \mathbf{c}_i^* (2J_j - K_j) \mathbf{c}_i + \delta \mathbf{c}_j^* (2J_i - K_i) \mathbf{c}_j + \mathbf{c}_i^* (2J_j - K_j) \delta \mathbf{c}_i + \mathbf{c}_j^* (2J_i - K_i) \delta \mathbf{c}_j] \quad (1.148)$$

$$\delta E = 2 \sum_i (\delta \mathbf{c}_i^*) \left[\mathbf{H} - \sum_j (2\mathbf{J}_j - \mathbf{K}_j) \right] \mathbf{c}_i + 2 \sum_i (\delta \mathbf{c}_i^\dagger) \left[\bar{\mathbf{H}} - \sum_j (2\bar{\mathbf{J}}_j - \bar{\mathbf{K}}_j) \bar{\mathbf{c}}_i \right] \quad (1.149)$$

$$\delta E = 2 \sum_i (\delta \mathbf{c}_i^*) \mathbf{F} \mathbf{c}_i + 2 \sum_i (\delta \mathbf{c}_i^\dagger) \bar{\mathbf{F}} \bar{\mathbf{c}}_i \quad (1.150)$$

therefore in varying the orbitals

$$(\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j + \mathbf{c}_i^* \mathbf{S} (\delta \mathbf{c}_j) = 0 \quad (1.151)$$

$$(\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j + (\delta \mathbf{c}_j^\dagger) \bar{\mathbf{S}} \bar{\mathbf{c}}_i = 0 \quad (1.152)$$

$$- 2 \sum_{ij} (\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j \epsilon_{ji} - \sum_{ij} (\delta \mathbf{c}_j^\dagger) \bar{\mathbf{S}} \bar{\mathbf{c}}_i \epsilon_{ji} = 0 \quad (1.153)$$

$$- 2 \sum_{ij} (\delta \mathbf{c}_i^*) \mathbf{S} \mathbf{c}_j \epsilon_{ji} - \sum_{ij} (\delta \mathbf{c}_i^\dagger) \bar{\mathbf{S}} \bar{\mathbf{c}}_j \epsilon_{ij} = 0 \quad (1.154)$$

one gets

$$\delta E' = 2 \sum_i (\delta \mathbf{c}_i^*) \left(\mathbf{F} \mathbf{c}_i - \sum_j \mathbf{S} \mathbf{c}_j \epsilon_{ji} \right) + 2 \sum_i (\delta \mathbf{c}_i^\dagger) \left(\bar{\mathbf{F}} \bar{\mathbf{c}}_i - \sum_j \bar{\mathbf{S}} \bar{\mathbf{c}}_j \epsilon_{ij} \right) \quad (1.155)$$

One comes to the final result of this groundbreaking paper[16]. Where the Fock matrix F is the hamiltonian that includes the mean field contribution from the previous iteration. Matrix $\mathbf{c}$ is the matrix of coefficients that constitutes the manybody wavefunction and has the dimension of the number of basis elements in both directions. $\mathbf{S}$ is the overlap matrix, which is diagonal in case of an orthogonal matrix. In solving the eigenvalue problem the respective eigenvalues of the Fock operator appear as the diagonal elements of ϵ .

$$\mathbf{F} \mathbf{c} = \epsilon \mathbf{S} \mathbf{c} \quad (1.156)$$

$$(\mathbf{F} - \epsilon \mathbf{S}) \mathbf{c} = \mathbf{0} \quad (1.157)$$

So one sets the procedure to diagonalise $\mathbf{F}$ enumerating the $\mathbf{c}$ which then gives rise to the density that changes $\mathbf{F}$. This is iterated until self-consistency.

when the Hartree-Fock equations are solved and self-consistency is reached the eigenvectors of the Fock operator can be ordered in increasing energy eigenvalue. The states are then occupied from bottoms up and are antisymmetrised by means of a Slater determinant.

2 The system of nanotubes

Overview The previous section demonstrated in detail how one is able to obtain the spectrum of energy eigenvalues and their corresponding state eigenvectors for a system of a single electron in an atom^{1.2}, in a dimer^{1.3} and in a periodic potential^{1.5}. One could be reminded of the the importance of boundary conditions, periodic for instance, and how they give rise to bounds of the spectrum. Then it became clear that the spectrum in terms of Fourier modes would describe the same system in a more compact way. One is able to perform such Fourier transformation with respect to each symmetry of the system, thus decoupling the modes corresponding to different symmetries. The number of modes for a given symmetry is equivalent to the number of irreducible representations corresponding to that symmetry group. This section describes the formulation of the Hartree-Fock Roothaan equations in terms of the underlying helical symmetry of the nanotubes.

2.1 Symmetries of Carbon Nanotubes

A so called “Nanotube” crystal corresponds to a tubule consisting of one or several concentric rolled atomic mono-layer sheets. Though the underlining method is in general invariant to the composition of the monolayer, this particular study focused exclusively on carbon nanotubes formed of honeycomb lattice monolayers. More specifically, only the systems of single wall carbon nanotubes (SWCN) were considered. As it will demonstrated below there are infinitely many ways to roll a single sheet, not only in terms of the radius but also in terms of the helicity. There is one to one correspondence of the helicity to the helical vector $\mathbf{R}(n_1, n_2)$, which is a function of discrete indices corresponding to the translations along the unit vectors of the mono-layer.

From Graphene to Nanotube

Now consider a honeycomb lattice, depicted below.

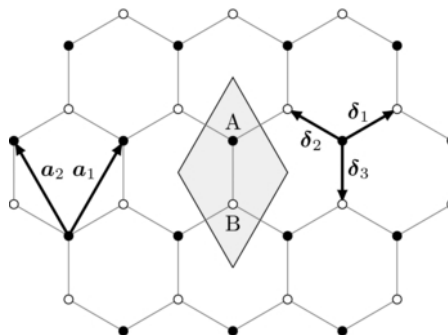


Figure 2.1: lattice adapted from M Eliashvili, G I Japaridze and G Tsitsishvili

No primitive lattice vectors exist such that translations by which would map the whole lattice and no other points. For instance translating twice with vector δ_3 results in a point that does not belong to the lattice, the centre of a hexagon. This lattice can be regarded as formed of two independent sub-lattices for which such primitive vectors exist. In fact the same lattice vectors would do, for both sub-lattices. Then if a unit cell includes one site of both sub-lattices,

A and B, it is true that all sites can be mapped by consecutive translations by the sub-lattice primitive vectors a_1, a_2 . Note that the unit cell spanned by the vectors a_1, a_2 forms a rhombus($\diamond$) with corners located at centres of hexagons. If one sets the origin at the centre of one of the hexagons, then the consecutive application of translations by a_1, a_2 to the unit cell tiles the plane completely.

Such planar lattice can be rolled to form a tubule called a nanotube. Therefore the structure of carbon nanotubes inherits much of its form from the structure of graphene. This can be done in many ways. In fact there exists a conformal one to one map all of the atoms of the nanotube from the atoms of the graphene as long as the usual boundary conditions of rolling was met. The corresponding constraint is

$$\mathbf{R}(n_1, n_2) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 = \left(n_1 - \frac{1}{2}n_2, \frac{\sqrt{3}}{2}n_2 \right) \quad (2.1)$$

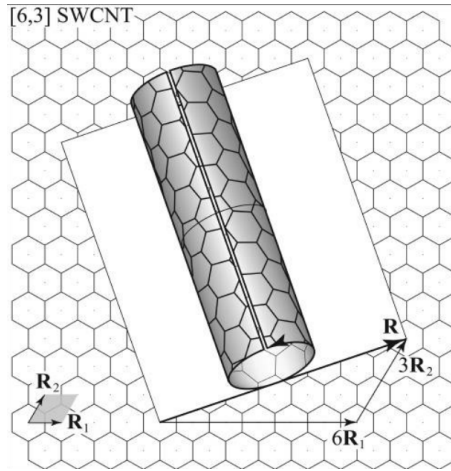


Figure 2.2: Vectors $\mathbf{R}_1, \mathbf{R}_2$ correspond to vectors $\mathbf{a}_1, \mathbf{a}_2$ respectively. Adapted from White, Mintmire[17]

Simple model For a sufficiently large nanotube, this model assumes that the nanotube structure is locally equivalent to the one of graphene. Therefore the bands are obtained simply by imposing by a periodic boundary condition along the circumference.

$$\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}) \quad (2.2)$$

$$\exp(i\mathbf{k} \cdot \mathbf{R}) = 1 \quad (2.3)$$

This implies one of the two wavevectors becomes discrete $K = \frac{2\pi i}{R}; i \in Z$ and the other, k , remains continuous. This is the result of folding the principal circumferential vector into the first Brillouin zone as demonstrated on a picture below.

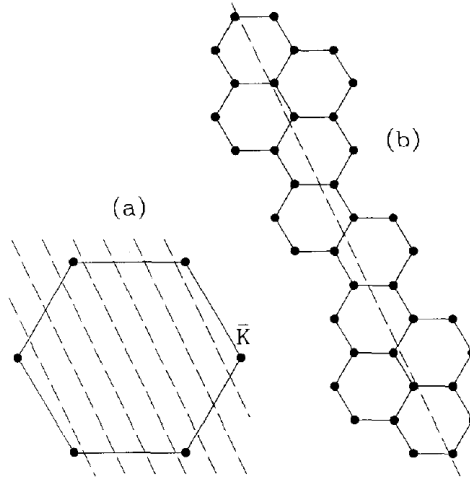


Figure 2.3: Adapted from White and Mintmire[17]

The band structure then depends crucially whether or not it touches the Dirac points of the 2D graphene sheet. This can be understood by considering

$$\exp(i\mathbf{K} \cdot \mathbf{R}) = \exp\left[\frac{2\pi i}{3}(n_1 + n_2)\right] = \exp\left(i\frac{2\pi\nu}{3}\right) \quad (2.4)$$

$$\exp(i\mathbf{K}' \cdot \mathbf{R}) = \exp\left[\frac{-2\pi i}{3}(n_1 + n_2)\right] = \exp\left(-i\frac{2\pi\nu}{3}\right) \quad (2.5)$$

where ν is an integer which is either 0 or ± 1 .

According to Ando et al. the condition for one of the bands of the nanotube to cross either Dirac point is if the the sum of the helical indexes is divisible by three[18].

Geometry Now, one can describe SWCNTs in terms of conformal mapping of the graphene onto the surface of a cylinder [17]. In order maintain the translational invariance, the graphene must be fold along certain $\mathbf{R}$, such that graphene sites $\mathbf{R}$ apart map onto themselves. Within this model and arbitrary SWCNT can be described in terms of $\mathbf{R}$ and the spacing between the C-C. To extend this analysis to the case of nanotube one has to include two additional symmetry operations that leave the system invariant. One being the second translation along the planar lattice, the second being associated with the wrap of the sheet represented by N-fold rotation in case of armchair and zigzag tubes and screw symmetry in case of the chiral ones. that constitutes of sites that are indistinguishable in terms of the geometry of the system. Therefore the local behavior in the vicinity of those sites is invariant under the translation to any other site. One can describe the Bravais lattice as the discrete array of sites situated at all possible Bravais vectors $\mathbf{R}$ with respect to the origin. In general, one can define the Bravais vector $\mathbf{R}$ in terms of discrete combination of primitive lattice vectors R_1, R_2 . Further description is provided in the following section.

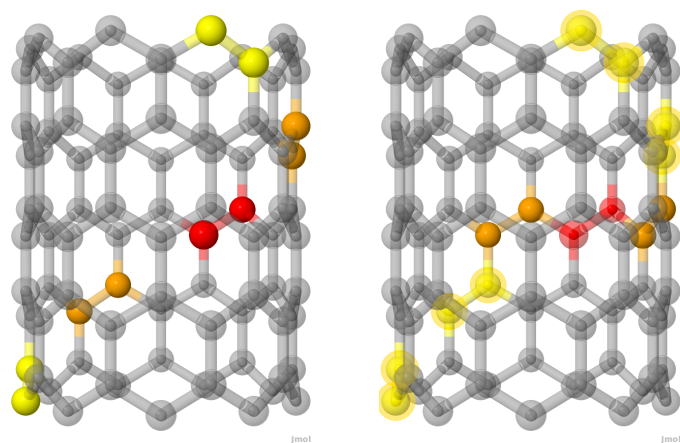


Figure 2.4: Left: red unit cell transformed by screw operation into orange and further to yellow cells. Right: Red unit cell transformed by N-fold rotation to the orange unit cells

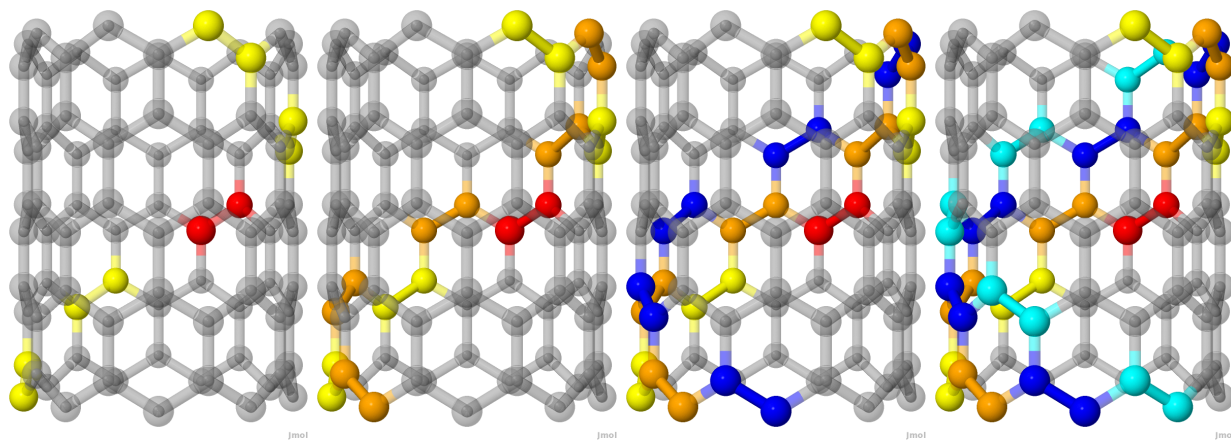


Figure 2.5: Rotation of the basic helix to form the whole supercell

2.2 Fourier Modes, Block Diagonalisation

This section describes the process of reformulation of the abovementioned Hartree-Fock LCAO equations for molecules or small to the form suitable for periodic systems. The main purpose of this reformulation is to accommodate the translational, rotational and point symmetry properties into the Hamiltonian of the SCF. This implies the correct transformation of all relevant one-body and two-body terms under the symmetry transformations. Also as will become obvious upon the reformulation, the expression of infinite series of the Coulomb and the Exchange integrals will be truncated using very general yet elegant concepts. At last since the Fock matrix will be expressed in terms of the reciprocal $\mathbf{k}$ vectors it is necessary to describe how the integrals will be performed in that particular basis. Generally speaking, the reciprocal basis will capture the energy contributions due specific fourier modes instead of particular two site interaction contribution. This will inevitably lead to block diagonalisation of the Fock matrix on the grounds that the contributions arising from two pairs of equally distant sites will contribute only to one mode. This is true for all pairs of sites related by certain symmetry. Therefore the particular direct space location of the sites does not matter, only the symmetry operation that maps one site into the other. This leads to a natural separation of the contributions into a block diagonal form that drastically reduces the difficulty of the problem at hand.

Cyclic Cluster Model

A well established approach used by many computational chemists is to represent the bulk by a possibly large cluster which is a cut-out of the solid. Such a cluster is finite, and even if it is constructed from formally equal units, the effect of the boundary is too strong near the center of the cluster. Consequently, the convergence of a calculated property with the size of the cluster towards the bulk limit may be extremely slow. This is often complicated by the necessity to saturate the boundary bonds (e.g. by hydrogen atoms or other terminal groups), which again changes the picture of the electronic structure. Since we are primarily interested in (pseudo)two-dimensional systems, let us restrict our considerations to those.

Let us assume a cluster constructed from a chosen atomic structure - the unit cell - by replicating the latter N_1 , N_2 -times in two respective lattice vector directions $\mathbf{a}_1$, $\mathbf{a}_2$. Thus, the cluster is built from $N = N_1 \cdot N_2$ unit cells which basically differ in their surroundings. Of course, in a periodic system, which we want to model, all the unit cells have equal surroundings. The idea behind the cyclic cluster approach is to impose such an equal surroundings to all of the units in the constructed cluster. In one dimension this resembles a ring which, in the infinite limit, changes to a translationally periodic chain.

Having a translationally periodic structure allows to transform the atomic orbital basis ($|p^{\mathbf{R}}\rangle$) to periodic Bloch orbitals

$$|p^{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |p^{\mathbf{R}}\rangle \quad (2.6)$$

whose linear combinations are known as the crystal orbitals (CO)[19] - i. e. periodic counterparts of the molecular orbitals. In (2.6)

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 \quad (2.7)$$

and $|p^{\mathbf{R}}\rangle$ means an atomic orbital in a unit cell defined by the translation $\mathbf{R}$. $\mathbf{k}$ is the reciprocal vector given as

$$\mathbf{k} = \frac{m_1}{N_1}\mathbf{b}_1 + \frac{m_2}{N_2}\mathbf{b}_2 \quad (2.8)$$

where the reciprocal lattice vectors $\mathbf{b}_j$ fulfill $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, with δ_{ij} being the Kronecker-delta. n_i, m_i in (2.7,2.8) are integer numbers. It is natural (though mathematically not inevitable) to take the central unit of the cluster as the reference one, hence for odd N_i we can use a convention

$$m_i, n_i = -(N_i - 1)/2, \dots, 0, \dots, (N_i - 1)/2 \quad (i=1, 2).$$

Obviously with increasing N_i one approaches the bulk. Hence, for $N_i \rightarrow \infty$ (bulk limit) the translational symmetry is guaranteed. Instead, for a finite cluster, a ring periodicity is imposed by

$$\mathbf{R} + \mathbf{R}' = \sum_{i=1}^2 \left\{ n_i + n'_i - N_i \cdot \text{int} \left(\frac{2(n_i + n'_i)}{N_i} \right) \right\} \mathbf{a}_i. \quad (2.9)$$

$\text{int}()$ is the integer part. Due to (2.9), any translation given as a sum of two translations within a cluster is again returned to the given cluster. Relation (2.9) corresponds to what is known as the Born - von Karman periodic boundary condition (PBC). In order that each unit cell experiences the surroundings of the reference cell we require

$$\langle p^{\mathbf{R}+\mathbf{R}'} | q^{\mathbf{R}'} \rangle = \langle p^{\mathbf{R}} | q^{\mathbf{0}} \rangle = S_{pq}^{\mathbf{R}\mathbf{0}} \quad (2.10)$$

$$\langle p^{\mathbf{R}+\mathbf{R}'} | \hat{h} | q^{\mathbf{R}'} \rangle = \langle p^{\mathbf{R}} | \hat{h} | q^{\mathbf{0}} \rangle = h_{pq}^{\mathbf{R}\mathbf{0}} \quad (2.11)$$

$$\langle p^{\mathbf{R}_1+\mathbf{R}'} q^{\mathbf{R}_2+\mathbf{R}'} | \hat{g} | r^{\mathbf{R}'} s^{\mathbf{R}_3+\mathbf{R}'} \rangle = \langle p^{\mathbf{R}_1} q^{\mathbf{R}_2} | \hat{g} | r^{\mathbf{0}} s^{\mathbf{R}_3} \rangle \quad (2.12)$$

with $\hat{h}, \hat{g}$ the one- and two-electron parts of the Hamiltonian, respectively. Any $\mathbf{R}$ is defined by (2.7) and $\mathbf{0}$ ($n_1=n_2=0$) refers to the reference (computational) unit cell.

Evidently, (2.11,2.12) are not valid for a finite cluster. Imposing surroundings of the reference unit to all units in the cluster means to replace the integrals at l.h.s of Eqs. (2.11,2.12) with the values of r.h.s.. For unambiguous assignments we must require:

$$S_{pq}^{\mathbf{0}\mathbf{R}} = S_{pq}^{-\mathbf{R}\mathbf{0}}, \quad (2.13)$$

$$h_{pq}^{\mathbf{0}\mathbf{R}} = h_{pq}^{-\mathbf{R}\mathbf{0}}, \quad (2.14)$$

$$\begin{aligned} \langle p^{\mathbf{R}_1} q^{\mathbf{R}_2} | \hat{g} | r^{\mathbf{0}} s^{\mathbf{R}_3} \rangle &= \langle p^{\mathbf{0}} q^{\mathbf{R}_2-\mathbf{R}_1} | \hat{g} | r^{-\mathbf{R}_1} s^{\mathbf{R}_3-\mathbf{R}_1} \rangle \\ &= \langle p^{\mathbf{R}_1-\mathbf{R}_2} q^{\mathbf{0}} | \hat{g} | r^{-\mathbf{R}_2} s^{\mathbf{R}_3-\mathbf{R}_2} \rangle = \langle p^{\mathbf{R}_1-\mathbf{R}_3} q^{\mathbf{R}_2-\mathbf{R}_3} | \hat{g} | r^{-\mathbf{R}_3} s^{\mathbf{0}} \rangle. \end{aligned} \quad (2.15)$$

While for the overlap (2.13) is always valid, for exact Hamiltonian Eq. (2.14) is exactly fulfilled for finite clusters with a center of symmetry, and, of course, for an infinite bulk. For sufficiently large clusters, an average of the two values may serve for this matrix element, in particular in non-polar systems. (2.15) are trivially valid for two-center two-electron integrals. Using (2.9) it is obvious that (2.15) are not generally fulfilled for three- and four-center two-electron integrals that occur in the full ab initio Fock matrix construction.

In addition to the aforementioned equalities, the same must hold for one-electron density matrix ($\mathbf{P}$), i. e.

$$P_{pq}^{\mathbf{0}\mathbf{R}} = P_{pq}^{-\mathbf{R}\mathbf{0}}, \quad (2.16)$$

Obviously, for any one-particle matrix element

$$O_{pq}^{-\mathbf{R}\mathbf{0}} = O_{qp}^{\mathbf{R}\mathbf{0}}. \quad (2.17)$$

Roothan Equations in the Cyclic Cluster Model

At the moment let us assume that we have at hand the density matrix $\mathbf{P}$. (2.11) is valid for any one-particle operator, hence we merely need to evaluate corresponding matrix elements of the Fock matrix in direct space, i. e. for closed shell system

$$F_{pq}^{\mathbf{R}\mathbf{0}} = h_{pq}^{\mathbf{R}\mathbf{0}} + \sum_{rs} \sum_{\substack{\mathbf{R}_1, \mathbf{R}_2 \\ (\mathbf{R}_3 = \mathbf{R}_1 - \mathbf{R}_2)}} [2(p^{\mathbf{R}}q^{\mathbf{0}}|r^{\mathbf{R}_1}s^{\mathbf{R}_2}) - (p^{\mathbf{R}}s^{\mathbf{R}_2}|r^{\mathbf{R}_1}q^{\mathbf{0}})] P_{rs}^{\mathbf{R}_3\mathbf{0}}. \quad (2.18)$$

Here, we have used

$$(pq|rs) = \langle pr|\hat{g}|qs\rangle. \quad (2.19)$$

If M is the number of basis functions centered on atoms within the reference unit cell, the full Fock matrix dimension in the direct space for the constructed cyclic cluster would be $N^2 * M^2$ and so would be the dimensions of $\mathbf{S}$ and $\mathbf{P}$. In principle these can be used in the Roothan equation ([20]), but in most realistic cases this would lead to prohibitively large matrix to be diagonalized.

Having (2.11,2.12) fulfilled permits transformation of the usual Fock matrix to Bloch basis,

$$F_{pq}^{\mathbf{k}\mathbf{k}'} = \delta_{\mathbf{k}\mathbf{k}'} F_{pq}^{\mathbf{k}} = \sum_{\mathbf{R}}^N e^{i\mathbf{k}\cdot\mathbf{R}} F_{pq}^{\mathbf{R}\mathbf{0}}, \quad (2.20)$$

which leads to factorizing the problem into N blocks of the dimension $M \times M$, i. e. for each $\mathbf{k}$ we solve the Roothan equation:

$$(\mathbf{F}^{\mathbf{k}} - \epsilon \mathbf{S}^{\mathbf{k}}) \mathbf{c}^{\mathbf{k}} = \mathbf{0}. \quad (2.21)$$

At the beginning one can easily assure that the outset of Bloch orbitals is orthogonal and hence diagonalisation of $\mathbf{F}^{\mathbf{k}}$ provides the crystal orbitals ($\mathbf{c}^{\mathbf{k}}$) for the given $\mathbf{k}$ -point symmetry. Unlike in a direct space, we have to deal with complex matrices.

Now, for a given $\mathbf{k}$, the density matrix can be easily expressed as

$$P_{pq}^{\mathbf{k}} = \sum_m^{occ} (c_{pm}^{\mathbf{k}})^* c_{qm}^{\mathbf{k}} \quad (2.22)$$

where $c_{pm}^{\mathbf{k}}$ are the occupied crystal orbitals coefficients for the given $\mathbf{k}$ -point symmetry. Finally, $\mathbf{P}^{\mathbf{k}}$ is back transformed to the direct space

$$P_{pq}^{\mathbf{R}\mathbf{0}} = \frac{1}{N} \sum_{\mathbf{k}}^N e^{i\mathbf{k}\cdot\mathbf{R}} P_{pq}^{\mathbf{k}} \quad (2.23)$$

and used for the calculation of the new Fock matrix until self consistency is reached.

In each iteration the energy per unit cell is then calculated as

$$E_{cell} = \sum_{p,q} P_{pq}^{00} (h_{pq}^{00} + F_{pq}^{00}) + \sum_{\mathbf{R} \neq 0} \sum_{p,q} P_{pq}^{\mathbf{R}0} (h_{pq}^{\mathbf{R}0} + F_{pq}^{\mathbf{R}0}) + E_{cell}^{nuc} \quad (2.24)$$

where E_{cell}^{nuc} is nuclear repulsion contribution

$$E_{cell}^{nuc} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|\mathbf{r}_{AB}|} + \sum_{\mathbf{R} \neq 0} \sum_{A,B} \frac{Z_A Z_B}{|\mathbf{R} + \mathbf{r}_{AB}|}. \quad (2.25)$$

In practical implementation the transformations from direct to $\mathbf{k}$ -space and *vice versa* are easily realized using the Euler relation

$$Re(F_{p \geq q}^{\mathbf{k}}) = F_{p \geq q}^{00} + \sum_{\mathbf{R} \neq 0}^{(N-1)/2} \cos(\mathbf{kR}) (F_{p \geq q}^{\mathbf{R}0} + F_{p \geq q}^{-\mathbf{R}0}) \quad (2.26)$$

$$Im(F_{p > q}^{\mathbf{k}}) = \sum_{\mathbf{R} \neq 0}^{(N-1)/2} \sin(\mathbf{kR}) (F_{p > q}^{\mathbf{R}0} - F_{p > q}^{-\mathbf{R}0}) \quad (2.27)$$

$$P_{p \geq q}^{\mathbf{R}0} + P_{p \geq q}^{-\mathbf{R}0} = \frac{2}{N} \sum_{\mathbf{k}}^{(N+1)/2} n \cdot \cos(\mathbf{kR}) Re(P_{p \geq q}^{\mathbf{k}}) \quad (2.28)$$

$$P_{p > q}^{\mathbf{R}0} - P_{p > q}^{-\mathbf{R}0} = \frac{2}{N} \sum_{\mathbf{k}}^{(N+1)/2} n \cdot \sin(\mathbf{kR}) Im(P_{p > q}^{\mathbf{k}}) \quad (2.29)$$

where $n=1$ for $\mathbf{k} \equiv (0,0)$, and $n=2$ for all other cases. From the last two equations, one easily obtains $P_{pq}^{\mathbf{R}0}$.

Having the cluster "saturated", i. e. if the results do not change with its further extension, we can safely assume that the density matrix corresponds to the bulk limit, as well as the Fock matrix constructed from it.

2.3 Helical Symmetry for Band Structure Calculations

The basic idea of accounting for the helical symmetry in nanotubes as suggested in [17]. The implementation is followed as given in [21] that is extended for full ab initio treatment within the Roothan approach closely related to that described above.

In general, any nanotube with a periodic structure can be constructed by rolling up a single sheet of a two-dimensional structure that is finite in one translation and infinite in the other one. We shall restrict ourselves to nanotubes created from two-dimensional hexagonal lattice characterized by two equivalent primitive translational vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ ($|\mathbf{a}_1| = |\mathbf{a}_2|$) that contain an angle of $2\pi/3$. Due to our convention, the dimension along the direction of $\mathbf{a}_1$ will be treated as finite, whereas infinite number of translations is assumed along $\mathbf{a}_2$. A nanotube characterized by a general helical (chiral) vector (m_{a_1}, m_{a_2}) is then created from the sheet that has m_{a_1} translations $(0, \dots, m_{a_1} - 1)$ along $\mathbf{a}_1$ and infinite number of translations along $\mathbf{a}_2$. Such

a ribbon is rolled up on a cylinder with the diameter:

$$d_{\text{NT}} = |m_{a_1} \mathbf{a}_1 + m_{a_2} \mathbf{a}_2| / \pi,$$

which follows from the fact the helical vector $m_{a_1} \mathbf{a}_1 + m_{a_2} \mathbf{a}_2$ is rolled up perpendicular to the rotation axis and makes the circumference of the cylinder. The irreducible computational unit cell corresponds to that in the two-dimensional structure except for the geometry relaxation due to the curvature. Exactly as in the two-dimensional structure that is infinite in both dimensions, each such unit experiences the same environment. Original translations along $\mathbf{a}_1$ and $\mathbf{a}_2$ are now transformed to roto-translations ($\hat{\mathcal{T}}_{a_1}$, $\hat{\mathcal{T}}_{a_2}$) characterized by the pair of operations $(\mathbf{z}_{a_1}, \varphi_{a_1})$ and $(\mathbf{z}_{a_2}, \varphi_{a_2})$, where $\mathbf{z}_{a_1}$, $\mathbf{z}_{a_2}$ are projections of $\mathbf{a}_1$ and $\mathbf{a}_2$ onto the axis of the nanotube, respectively, and φ_{a_1} , φ_{a_2} are rotation angles related to those translations. Hence, for any point defined in a cylindrical coordinate system (ρ, ϕ, z) ,

$$\hat{\mathcal{T}}_i(\rho, \phi, z) \equiv (\rho, \phi + \varphi_i, z + \mathbf{z}_i) \quad \text{for } i = a_1, a_2.$$

If we relate pseudovectors $\mathbf{t}_i$ to these roto-translations, in analogy with the two-dimensional planar lattice we can define reciprocal pseudovectors $\bar{\mathbf{t}}_i$ such that

$$\bar{\mathbf{t}}_i \mathbf{t}_j = 2\pi \delta_{ij}.$$

Let the atomic orbital χ_{j_a, j_b} be a counterpart of the reference unit cell atomic orbital $\chi_{0,0}$ in the unit cell defined by $\hat{\mathcal{T}}_{a_1}^{j_{a_1}}$ and $\hat{\mathcal{T}}_{a_2}^{j_{a_2}}$ roto-translations. The structure created by m_{a_1} roto-translations $\hat{\mathcal{T}}_{a_2}$ (including 0) of the reference computational cell can be treated as an ideal cyclic cluster with periodic boundary conditions, since, indeed, in the nanotube each unit has an equivalent surrounding. Consequently, from m_{a_1} atomic orbitals $\chi_{j_{a_1}, 0}$ ($j_{a_1} = 0, m_{a_1} - 1$) one can create m_{a_1} symmetry orbitals:

$$\chi^{\mathbf{k}_{\phi r}} = \frac{1}{\sqrt{m_{a_1}}} \sum_{j_{a_1}=0}^{m_{a_1}-1} e^{i\mathbf{k}_{\phi r} \cdot \mathcal{R}_{j_{a_1}}} \chi_{j_{a_1}, 0},$$

where $\mathcal{R}_{j_{a_1}} = j_{a_1} \mathbf{t}_{a_1}$ and there are m_{a_1} allowed discrete values of $\mathbf{k}_{\phi r} = \frac{r}{m_{a_1}} \bar{\mathbf{t}}_{a_1}$ for $r = 0, m_{a_1} - 1$. These symmetry orbitals are propagated due to the $\hat{\mathcal{T}}_{a_2}$ to infinity providing Bloch orbitals:

$$\chi^{(\mathbf{k}_{tr}, \mathbf{k}_{\phi r})} = \lim_{N \rightarrow \infty} \frac{1}{\sqrt{m_{a_1} \cdot N}} \sum_{j_b=-N/2}^{N/2} \sum_{j_{a_1}=0}^{m_{a_1}-1} e^{i(\mathbf{k}_{tr} \cdot \mathbf{R}_{j_{a_2}} + \mathbf{k}_{\phi r} \cdot \mathcal{R}_{j_{a_1}})} \chi_{j_{a_1}, j_{a_2}},$$

where $\mathbf{R}_{j_{a_2}} = j_{a_2} \mathbf{t}_{a_2}$ and $\mathbf{k}_{tr}$'s are any values from the first Brillouin zone for the one-dimensional system. In the practical implementation into the codes that generate integrals in a cartesian coordinate systems, one has to take care for the appropriate rotation of the coordinate system for each basis function center to preserve the rotational symmetry.

The first set of calculations were centered about the investigation on how the variation of the magnitude of the lattice vector affects the total energy. In the process of doing so, the many-body eigenstate of the system has been determined by an exact diagonalisation. As described

above, in order to also account for the mean field created by the electrons themselves an iterative procedure must be implemented to tackle the problem that is no longer linear in the coordinates of electrons. Aiming for a full description of all electrons, whether valence or not, implies that the basis set per unit cell has to be at least of the size of twelve spinorbitals. Due to spin degeneracy, two spin orbitals can be generated from each orbital if occupied it in a singlet configuration. Since the system in question is (not) even a conventional closed shell system, it is not possible to use six orbitals only. Moreover, the lowest unoccupied band arising from the lowest unoccupied orbital is of great interest at least one more orbital. In fact, such iterative procedure requires even greater variational freedom, in order for it not to converge into a local minimum instead of the global one. Therefore, the minimal basis used in these calculations constitutes of five orbitals on each of the two atoms of the unit cell.

3 Analysis and discussion of results

Overview In this section the numerical procedures and the associated results are elaborated. Those results are then further analysed, or even form a basis of a simple model that is introduced to address the macroscopic behavior of the system. All macroscopic properties that are studied here can be classified into three categories, namely the category of energetic, elastic and electronic properties. In addition to the physical interpretation of the results, also the numerical aspects are addressed, such as the computational difficulty, convergence and computational cost of scaling of the system.

3.1 Energy and Convergence

In variational schemes, such as this one, the focus is put on the energy eigenvalue of the many-body system. The configuration of electrons is changed by varying the orbitals until a minimal value is of energy E_G is obtained. Each subsequent iteration yields a more precise result (unless the system is trapped in a local minimum). The criterion for convergence is the magnitude of the partial difference ΔE_n in energy of the last two iterations $n - 1$ and n . If this difference is smaller than a given threshold σ , the iteration procedure stops and the final energy is set to value of the energy of the last iteration, with the precision of the threshold.

$$\Delta E_n = |E_{n-1} - E_n| \tag{3.1}$$

$$if \Delta E_n \leq \sigma \tag{3.2}$$

$$E_0 = E_n \tag{3.3}$$

Naturally the number of the iterations n_{max} required for a given precision increases as the threshold σ decreases. A good measure of how a calculation converges is to consider how the partial difference ΔE_n evolves throughout iterations n . Even though this relation depends on details of the system such as the geometry, nevertheless general observations can be drawn from particular case of SWCN, of chirality $L = (6, 6)$ and super-cell length $s = 15$, considered below.

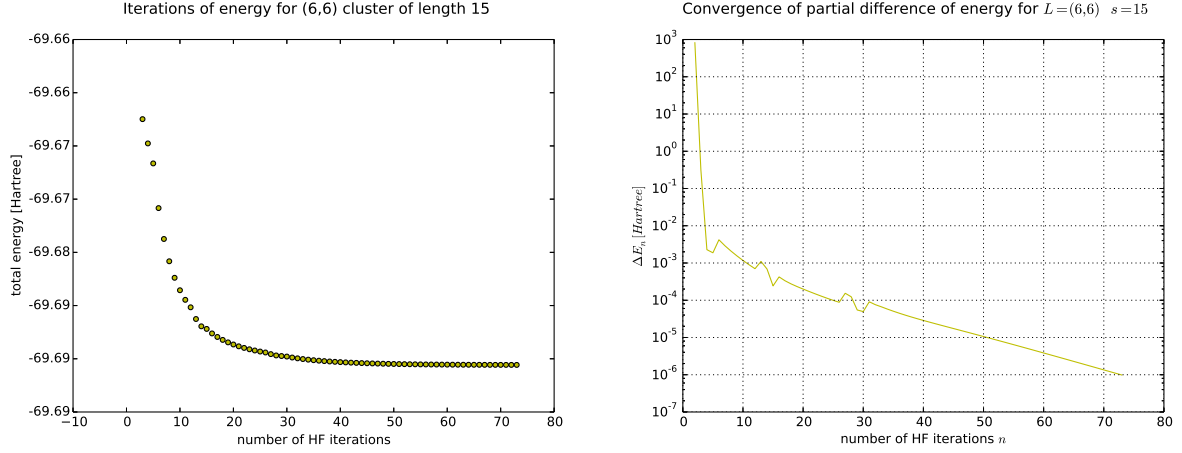


Figure 3.1: Total energy per cell versus lattice vector. The logarithmic scale depicts that it takes about 20 iterations to increase the precision by an order of magnitude.

The problem is initialised without a guess for the mean field of electrons and so in the first iteration the potential term consists only of Coulomb potential due the nucleons and no mean field of electrons. One can observe that it takes around two iterations, after the initialisation, for the energy to reach reasonable values. From there on, it is fair to say, that the number of required iterations n_{max} scales exponentially with the desired precision σ . This is justified by a linear shape of the partial difference ΔE_n on the logarithmic scale. This feature of exponential dependence remains true for the precision σ ranging from order 10^{-3} to 10^{-7} for systems of various geometry, converging to different energies at different pace. Whether this trend continues to be true in the limit $\lim_{\sigma \rightarrow 0}$ cannot be concluded, however increasing precision even further would hardly have a significant macroscopic effect.

Saturation of the mean field cluster

The calculation is performed on a cylindrical segment of a nanotube, within which one looks for electronic states that minimise the energy for the potential arising from protons. It is true that the total energy increases in magnitude as larger and larger segments are considered. Within the “super cell” the two body Coulomb interactions are calculated between all electrons, by means of the mean field. The size of this “super cell” is defined by the number of screw operations l that replicate the unit cell prior to applying the rotational symmetry. Generally the number of iterations n_{max} increases with l , but also the total energy E_{tot} is affected by the size of the super cell as more precise mean field is considered. The following case study investigates how sensitive the E_{tot} is to the length of the “super cell”. Also the relationship between the length l and the computational difficulty is explored. In each of the iterations the Hartree-Fock hamiltonian (Fock matrix) is diagonalised. Mind you that beside the number of iterations the computational difficulty depends on the size of the Fock matrix, which scales linearly with the length l . Diagonalisation time scales as the polynomial of order three with respect to the

dimension of the matrix.

$$\sim O(n^3) \quad (3.4)$$

The Fock matrix is a complex one but for real matrices, a dedicated routine in LAPACK library scales as

$$\sim \frac{4}{3}n^3 + O(n^2) \quad (3.5)$$

therefore usually this procedure is one of the bottlenecks for calculations involving many atoms. However due to the symmetry of the system the problem can be recast by means of the Fourier transformation. This decomposes the problem into the substantially smaller problems for each irreducible representation of the symmetry operation. Therefore the matrix size that is to be diagonalised does not depend any further on the size of the system. Gradual increase of the super-cell merely increases the number of sub-matrices into which the problem is decomposed.

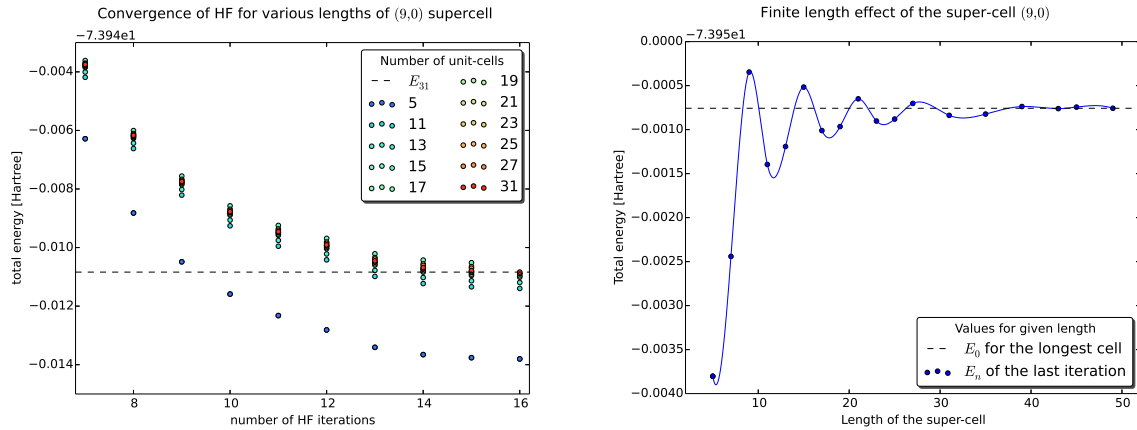


Figure 3.2: **Left:** The energy evolution in the process of converging HF, several cluster lengths are depicted. **Right:** the energy value of the final iteration for a given length of the cluster. Clearly from certain threshold length the energy has sufficiently converged to the same value as if the whole nanotube were considered for the HF.

Energetic properties

The figure below 3.1 depicts the energy decomposition of energy per unit cell calculated on the “super-cell” cluster. What is meant by the total energy E_{tot} (blue) is simply the sum of Coulomb energy necessary to assemble the crystal lattice (red) and the sum of the energy eigenvalues for all electrons within the super cell (green). Of course the electronic orbitals account for the mean-field term in the hamiltonian, because their configuration minimises the energy functional with respect to the orbital rotations.

$$\epsilon[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (3.6)$$

It was famously observed by Lanczos that any physical law, which can be expressed as such variational principle, describes a self-adjoint operator.

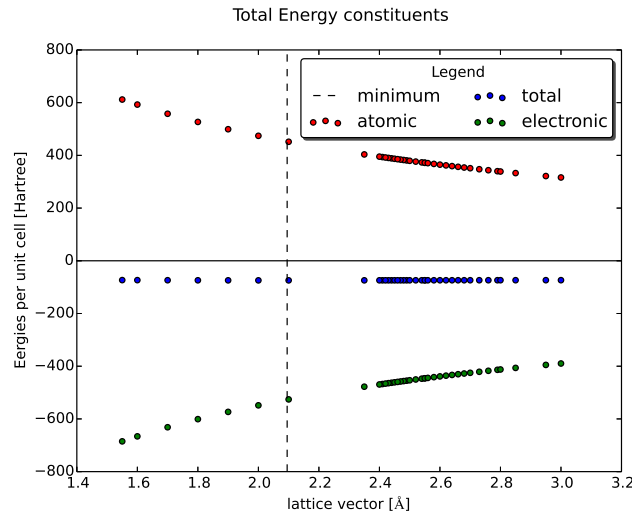


Figure 3.3: Constituents of energy are changed as the lattice vector is varied for a system of (3,2) using DZP basis. The minimum of total energy is found substantially lower than that of the graphene and also lower than the reference[22] for this chirality. This set of data was obtained from the first benchmarks of the code in which the DZP basis.

This serves as a good qualitative demonstration of the fact that a strain is introduced to a tube it would gradually shrink. Intuitively the the energy per cell of a large nanotube converges to the value of graphene. Any shorter radius results in strain energy defined as such

$$E_{st} = E_{tot} - E_{Gr} \quad (3.7)$$

Now consider an enumeration of this strain energy using method that doesn't utilise the helical symmetry.

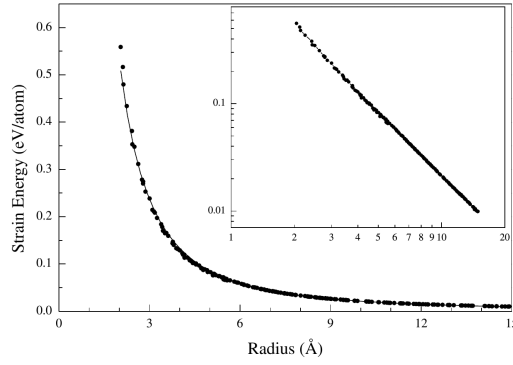
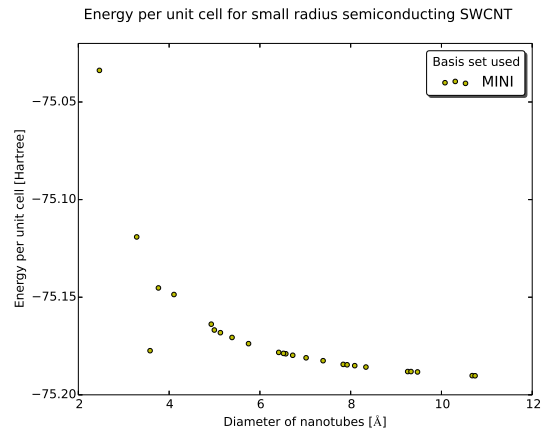
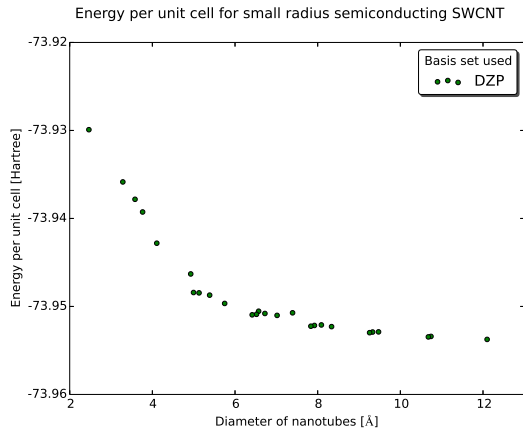


Figure 3.4: Adapted from the numerical study of SWCN by [22]. Clearly the strain increases logarithmically as the radius shrinks. Mind you that the each point represents a distinct chirality as opposed to shrinking the separation of a particular nanotube.

This figure is in a very good agreement with the set of semiconducting nanotubes of various chirality presented below. Here the graphene energy E_{Gr} would be the value to which the large tubes converge. We can see that not only the shape is recovered but also the width of the function is very accurate if one converts from Hartree. Interestingly there is a small shift of the total energy which is basis dependent. On the plot of values calculated with the MINI basis there lies an outlier for a diameter less than 3 . As mentioned above the very small radii are not very reliable and neither are observed in nature.



3.2 Vibrational properties

The carbon nanotube crystal structure consists of two distinct sub-lattices. Therefore the description of such system requires two carbon atoms in the unit cell. Each such atom possesses three degrees of freedom for three real space coordinates. Therefore, in general, the phonon dispersion relation will consist of $6N$ distinct phonon branches, where N is the number of unit cells considered. However if we are to insist on not breaking the crystal symmetries of the nanotube, only one such branch survives. For demonstrative purposes here we address the breathing mode results in scaling of the nanotube without breaking either rotational, translational or helical symmetries. Therefore now consider that the vector position of atoms on one sub-lattice are u_j .

Also consider the classical analogue of momentum

$$H_{clas.} = \frac{1}{2M}p^2 - \frac{1}{2}K(a - a_0)^2 = \frac{M}{2} \left(\frac{da}{dt} \right)^2 - \frac{1}{2}K(a - a_0)^2 \quad (3.8)$$

solve the differential equation by finding an optimum to the Hamiltonian

$$\frac{dH_{clas.}(a, \dot{a})}{dt} = \frac{2M}{2} \left(\frac{d^2a}{dt^2} \right) - \frac{2}{2}K(a - a_0) \frac{da}{dt} = Ma'' - Ka'(a - a_0) = 0 \quad (3.9)$$

$$a'' = \frac{K}{M} \quad (3.10)$$

so the frequency of such modes is 1.5

$$\omega = \sqrt{\frac{K}{M}} \quad (3.11)$$

Such description can be drawn about a system that oscillates near a local minimum of the total energy with respect to an arbitrary parameter. Then one can think of a force field associated with that potential and subject the state to a restoring force once out of the equilibrium. The force field is simply the derivative of the potential with respect to the parameter in question, and a particular value of that field is the returning force the state experiences. Mind you that the vector derivative guarantees that around minima the direction of the force always opposes the direction of the displacement. Generally speaking the field will not be a linear force field as it is the case in Hookian elasticity or simple harmonic oscillator. Lenard-Jones potential, for instance, gives rise to a polynomial field of a high rank. Nevertheless such field can always be extrapolated into a quadratic form, given that the system remains reasonably close to the equilibrium. In what follows the total energy of a particular carbon nanotube was calculated for a set of lattice vectors a_i . As described above the total energy constitutes the sum of electronic energy of electrons as well as the coulomb and exchange energy equivalent to the assembly of both electrons and nucleons. In calculating these energies for the set of lattice vectors no crystal symmetry was broken (neither the helical nor the rotational). Therefore the energy landscape is only one dimensional and can give rise only to the breathing mode, because all other nontrivial modes break crystal symmetries. Owing to this simple one body description, the dispersion relations will be constant and the system will vibrate in only one frequency. A more advanced

treatment reveals that the breathing mode very dependent on the helicity of the tube.

The figure below depicts the above-mentioned energy surface as the function of interlattice spacing of the hexagonal lattice.

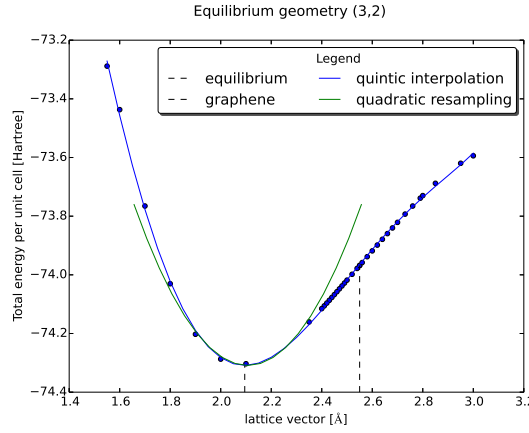


Figure 3.5: Total energy versus lattice vector

The blue line represents the interpolation of the enumerated energies in terms of a polynomial fit of rank 5, which minimises the deviation squared. Purposely the odd polynomial was chosen to capture the asymmetry of the curve that resembles the Lenard Jones potential. The equation of which is centered about origin of lattice vector $a = 0$ (therefore the linear term has significant magnitude).

$$E_5(a) = 1.188381(a)^5 - 13.351577(a)^4 + 57.514455(a)^3 - 116.401511(a)^2 + 107.033980a - 107.262648 \quad (3.12)$$

The first derivatives of which indicate the slope of such a curve

$$E'_5(a) = 5.941908(a)^4 - 53.406311(a)^3 + 172.543366(a)^2 - 232.803022a + 107.033980 \quad (3.13)$$

roots of which represent zero slopes and therefor local optima of the initial equation. This quartic equation yields four roots two of which are complex i.e. do not cross zero point.

$$\begin{aligned}
&2.960034 + 0.274613i \\
&2.960034 - 0.274613i \\
&2.095081 \\
&0.972926
\end{aligned} \tag{3.14}$$

It is clear that the one corresponding to the equilibrium position is the third one

$$a_0 = 2.095080 \tag{3.15}$$

Now it is straight-forward to expand the fitted polynomial in Taylor series around the the equilibrium value a_0 .

$$x = a - a_0 \tag{3.16}$$

$$a = x + a_0 \tag{3.17}$$

$$da = dx \tag{3.18}$$

$$E(a) \simeq E(a_0) + E'(a_0)x + \frac{E''(a_0)}{2}x^2 = E(a_0) + \frac{E''(a_0)}{2}x^2 = E_0 + cx^2 \tag{3.19}$$

$$E_0 = -74.308763eV \tag{3.20}$$

$$c = 2.745631Hartree^{-2} \tag{3.21}$$

However in doing this the terms in the polynomial that account for the asymmetric part far away from the equilibrium are taken into account and so they induce an error in the near equilibrium regime. To prevent this from happening the fifth polynomial in question is sampled in the small neighborhood around the equilibrium $a_0 \pm 0.5$ and then the best possible fit of the quadratic polynomial is found, again in terms of minimising the deviation squared. This is represented on figure [3.5] as the green line.

$$E_2(a) \simeq 2.708552(a)^2 - 11.413362(a) - 62.285492 \tag{3.22}$$

Then the equilibrium point needs to be reevaluated

$$\alpha_0 = 2.10691218 \tag{3.23}$$

and to align it the function is expanded around α_0

$$E_g = -74.308968 \tag{3.24}$$

$$c_2 = 2.708552 \text{ Hartree}^{-2} \simeq 2.71436 \cdot 10^{-18} \text{ J } 10^{20} \text{ m}^{-2} = 1.18 \cdot 10^3 \text{ kg s}^{-2} \quad (3.25)$$

so within this model of a linear force field one can examine how does the energy change when the magnitude of the unit vector is changed by x around the equilibrium geometry.

$$F(x) = -\frac{dE_g(x)}{d(x)} = -2c_2x = Kx \quad (3.26)$$

$$K = \frac{\partial^2 V}{\partial x^2} = m\omega_E^2 \quad (3.27)$$

$$\omega_E = \pm \sqrt{\frac{K}{m}} \quad (3.28)$$

in which the mass constitutes of two carbon atoms of molar mass $M = 12 \text{ g/Mol}$. So the mass of the two atoms is

$$m = \frac{2 \cdot 12 \text{ g}}{6.02 \cdot 10^{23}} \simeq 4 \cdot 10^{-23} \text{ g} = 4 \cdot 10^{-26} \text{ kg} \quad (3.29)$$

so the possitive frequency is equal

$$\omega_E = \sqrt{\frac{2 \cdot 1.18 \cdot 10^3 \text{ kg s}^{-2}}{4 \cdot 10^{-26} \text{ kg}}} = 2.42 \cdot 10^{12} \text{ s}^{-1} \quad (3.30)$$

out of which only the one of positive frequency is obtained.

now it needs to be understood that this stretching, due to increase of the unit vector, is isotropic and so it doesn't break the six-fold rotational symmetry. Therefore all of the constituent bonds are stretched the same. In order to obtain a proper dispersion relations a more involved microscopic model needs to be employed. One basically needs a description of single atoms in a lattice and the corresponding force fields among them. This is because no other mode than trivial exists within the simple harmonic oscillator. This problem in all its generality is extremely complicated as one needs to include all two body interactions, this means also among distant atoms. In the first approximation one can simplify the problem in two regards. First restricts the consideration only the interactions between the nearest neighbors and the second assumes the interaction between the nearest neighbors arising from a linear force field i.e. hookean elasticity. Therefore lets calculate the linear spring constant of the bond between the two carbons in the unit cell of a carbon nanotube. In one unit cell there are four shared bonds and out of which only one lies within the cell. On average there are three bonds stretched per unit cell. These bonds can be thought of as in the parallel regime and so be linked to the overall elastic constant K calculated above for the stretch of the whole unit cell. Therefore each the bond elastic constants are equal to

$$K = -2c_2 \quad \therefore \quad k_1 = k_2 = k_3 = -\frac{2}{3}c_2 = 1.805701 \text{ Hartree}^{-2} \quad (3.31)$$

For a more in depth approach those constants can be used to construct the phonon spectrum for the system of nanotube.

3.3 Electronic properties

The geometry of carbon nanotubes respects two distinct symmetries; the N fold rotational C_N and the screw symmetry S [23]. The number of irreducible representations of C_N for a given chiral vector $C(m,n)$ equals $N = m + 2n$. The screw symmetry maps the crystal back onto itself after applications of both translation and n -fold rotation operation. Since these two symmetry classes commute, each of them leads to Bloch's condition's of its own. Therefore in the Fourier space the final state will be characterised by a tensor product of two uncorrelated substates and so could be described by a two dimensional band structure. However unlike in case of a two dimensional layer here the second wavevector will take only as many discrete values as the number of irreducible representations of the C_N . The other index, arising from the helical symmetry will in principle take a countable infinite number of values. Since this project addresses only nanotubes of small diameter, the number of the rotational operation is rendered to be small. Moreover, due to point symmetry the forward rotation gives rise to the interatomic distances equivalent to those of backward rotation. Therefore the electronic hamiltonian is invariant to the direction of the rotation. This implies that the energy eigenvalues and eigenvectors and hence the bandstructure will be symmetric in the wave-vector index associated with the rotations. This decomposition can be studied for small radius nanotubes, such as (3,2), because of the small number of rotations under which the crystal structure of the nanotube is invariant. In this case it is five as one the smallest element of rotation is $\frac{2\pi}{5}$ radian. However number of irreducible representations, besides the identity i.e. null rotation, is just three because rotating forward is equivalent to the backward rotation. In Fourier space the energy contributions separate into the parts that arise from neighbors that are related by the same symmetry. For instance nearest neighbors contributions arise from application of rotation by $\frac{2\pi}{5}$ radian either forwards or backwards. Those form one band structure of their own and the macroscopic band structure would be equivalent to the linear superposition of those subbands. Depicted below is the spectral decomposition of the band structures with respect to the irreducible representations of the rotation operators of the super cell.

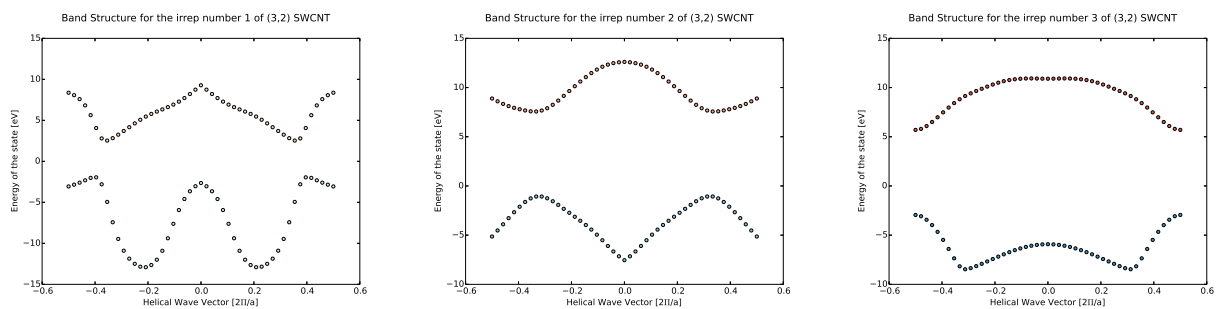


Figure 3.6: Three unique bandstructures corresponding to the irreps of C_5 operation. Two additional diagrams exist but are identical to the first two. The intensity of the colour corresponds the extent of rotation of the irrep. For instance Light blue and light red arise from a small rotation as opposed to the dark red and dark blue for which to rotation is close to π rad.

Bandgap classification Clearly the smallest direct bandgap appears at the first graph and therefore corresponds to the circumferential mode that is invariant under the that particular rotation. Then it is natural to set it equivalent to the the direct bandgaps of the global system. Closer inspection of the individual diagrams reveals that there is no substantially smaller indirect bandgab, one that describes the smallest energy difference between two bands for one spectral mode (diagram), but for which the helical wave vector can have distinct values for HOMO and LUMO bands. This sort for bandgap is referred to as indirect in k , and though not present in this particular case, it would correspond to the scattering process of an electron that involves the change of its wave vector. In analogy to this, a bandgap indirect in K can be considered, which corresponds to the smallest energy gap between the two bands for a fixed helical wave vector k but across all spectral modes K of the system. Such an energy corresponds to the transition of an electronic state in the mode K to the first excited state in another mode K' . At last if one relaxes constraints for both wave vectors K and k one obtains the most indirect bandgap which is here referred as the indirectest bandgap.

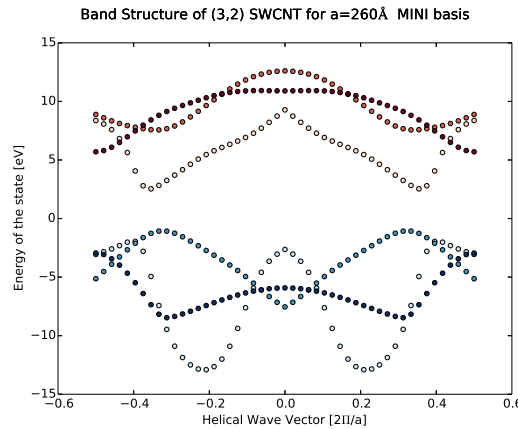


Figure 3.7: Projection of all sub-bands onto one plane. It is obvious that there exist a smaller bandgap than the direct one. It is the one between the light red HOMO (irrep. 1) and medium blue LUMO (irrep. 2)

Comparison with theoretical models For a sufficiently large nanotube a periodic boundary condition can be set along the circumference.

$$\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}) \quad (3.32)$$

which leads to the condition

$$\exp(i\mathbf{k} \cdot \mathbf{R}) = 1 \quad (3.33)$$

this leads to the wave vector along the circumference direction being discrete and the one dimensional bands being linear cuts of the full Brillouin zone. In fact the number of the bands is equivalent to the number of atomic orbitals times the number of carbon atoms in the first Brillouin zone. Again for sufficiently large tubes the zone is flat and locally identical to the

one of graphene. Due to the geometry of graphene's Brillouin zone for certain chiralities one of the wave-vectors crosses either Dirac's points K or K' . For uncorrelated systems those are places where LUMO and HOMO bands touch. There is a condition on the sum of chiral indexes $n + m = 3i$ to be divisible by three[18]. The tubes that satisfy this condition or the armchair condition $n = m$ are predicted to have one of the wavevectors that crosses the Dirac points. And therefore be metallic. Of course this is without considerations for the mean field and the curvature that are able to open the gap. Below two band structures are considered. The theory predicts both of them to be metallic, one by the virtue of being armchair, the other due to the sum of the chiral components being divisible by 3.

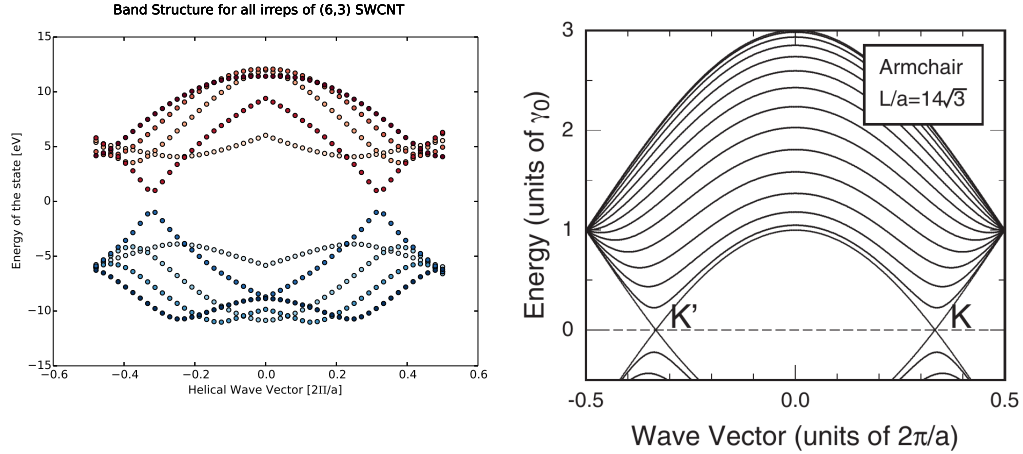


Figure 3.8: Bandstructure comparison between numerical evaluation of semimetallic (6,3) SWCNT and tight binding prediction of metallic (14,14) SWCN. The qualitative shapes of the bands as well as the locations of the Dirac points are in a good agreement. From the numerical calculations the corresponding energy parameter γ_0 could be estimated, for this case it would be around 5 eV. The diagram on the right is adapted from Ando et al. 2005[18].

limitations of accuracy Whether the true value of bandgap of (6,3) is exactly zero even in practice is not certain. If not it is very likely that it will be very small $\Delta\epsilon \ll 0.1\text{eV}$. Which is still one order of magnitude lower than what can be deduced from the diagram. The main reason for this is that there are few reciprocal points sampled in the Brillouin zone. If it would be more populated, including points corresponding to the remote parts of the tube, the vicinity of the Dirac's points would be described by many more points and band gap would certainly decrease, perhaps even to the point of near touch. This of course is not a problem because once the density has been converged, one knows the value of it even at very distant places due to periodical repetition. The other issue to stress is the amount of cells considered in the mean field. It has been shown how the energy converges as the cluster saturates, and it turns out to be the length corresponding to around 10 – 15 screw operations. However the armchair tubes are more difficult to saturate and therefore this may provide a reasonable explanation of the magnitude of their bandgaps.

Transition between the insulating and the conducting phase If one considers the lattice vector as the order parameter, then it is interesting to observe whether or not distinct phases exist as the order parameter is varied. In this case the phases that have a macroscopic consequence are how the nanotube behaves in terms of the conductivity. Therefore if the overall bandgap of the nanotube is greater than zero, or a small threshold, then the material is classified as insulator. If the bandgap is zero then it is a metal. From the perspective of conductivity, even more exotic phases exist, such as superconducting phase, but those are usually sub phases of those two, e.g. superconductor also being a metal.

It is logical to assume that if a metallic phase exists, then at some point there would be transition into the insulating state. This is guaranteed by the fact that infinitely distant sites have no overlap and therefore must per se. form an insulating phase. For a particularly small system (3,2) which is unlikely to be the preferred chirality in the process of growing, and might not even be a stable configuration, the band structures obtained are dependent on the choice of the finite basis set. This is likely to be an issue related to the particular basis and not to the routine itself. Nevertheless, even if it were true that the Double-Zeta basis set would not be working conveniently with the program, still one can extract some information about the behavior of the system before it would be investigated by more sensible calculations. One such general observation is that whether the nanotube is conducting or insulating depends not only on the chirality but also on lattice vector. It is likely that the static equilibrium, the configuration of smallest total energy, would be the proffered configuration of the system, however it is not clear whether the system would remain in such state even under charge transfer of non-negligible magnitude. Below you can see the conducting, semimetallic and metallic states for different order parameters, without thermal and vibrational considerations.

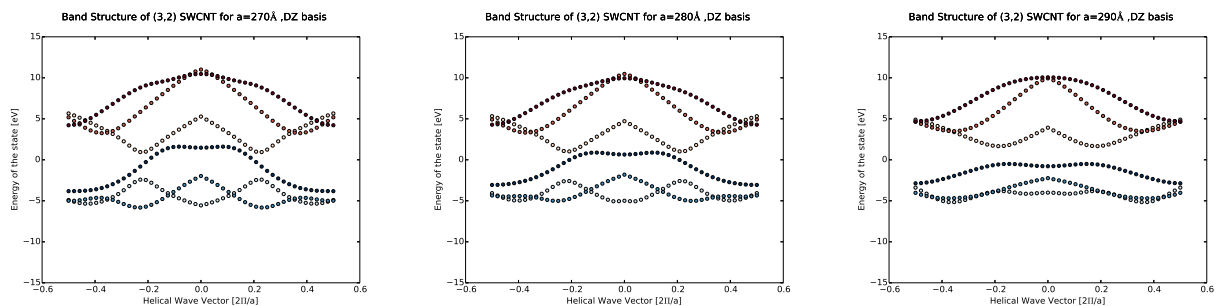


Figure 3.9: Variation of the band structure with the lattice spacing. This calculation was used as the first benchmark calculation with the Double-Zeta (Dunning) basis set. Even though the obtained energy values are consistent, the LUMO band of the first irrep. (dark blue) seems to have the wrong parity and predicts the nanotube to be metallic at the equilibrium. It is unclear if such small nanotubes do exist and therefore it is difficult to argue whether or not it'd be metallic at the equilibrium. However other quantities, such as the bandgap “direct in both K and k ” can be looked at. It is the gap between the light blue and light red bands. These are in a good agreement with the other basis. Therefore before further investigation takes place no other bandgaps are considered from this set of calculations.

Phase diagram Extending the idea of the previous paragraph, one can calculate band structures for many values of the lattice vector. At each of these lattice spacings one considers the differences of two out of ten bands for each symmetry representation. Since there are two distinct wave-vectors, all in all four combinations of bandgaps exist. Those are the smallest difference between two bands in one representation K i.e. either bangaps direct in both k and K or bandgaps direct in K , between bands of the same representation, but indirect k . Or between bands of different representations but for the same k , or indirect in both.

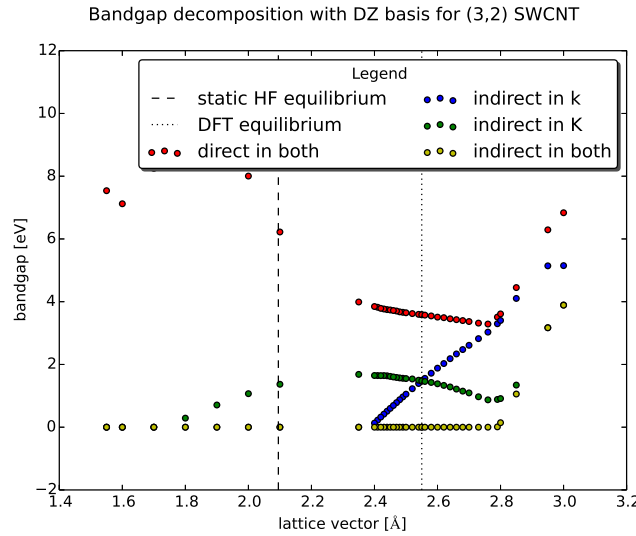


Figure 3.10: For (3,2) nanotube; the separation of the two atoms in the unit cell, i.e. the lattice vector, is varied around the reference DFT equilibrium[24]. Bandgaps represent shortest energy difference between HOMO and LUMO bands for a given freedom of helical wave-vector k and circumferential wave-vector K . Conventional direct bandgap would most closely resemble the green set, keeping the helical wave-vector k fixed, while allowing for the circumferential wave-vector K to change. Conventional indirect bandgap would resemble the bandgap indirect in both wave-vectors, the yellow set. This discrepancy lies in the projection of the helical vector to the direction along the tube, which is usually also the direction of the principal wave-vector k .

First observation is at large separations all bandgaps are non-zero and tend to increase with increasing lattice vector. Therefore for large separations the system behaves as an insulator. The second observation is that all bandgaps, except the one direct in both K and k , tend to zero as the order parameter decreases. This makes sense as on average the overlaps of the orbitals get higher and so it is more likely that the conduction is possible. The other feature is how many times those bands cross. It is obvious that the most indirect (yellow) and the most direct (red) will not cross any lines, at most touch. This is because all of the most direct bandgaps are considered within the more direct ones. Likewise the most indirect has the highest degree of freedom and so no other value is smaller. What is not obvious is that the lines that are indirect with respect to different wave-vectors (blue and green) cross once. However the most remarkable thing is that they cross at the reference value of the equilibrium that was used nowhere in the

program. It is true that the spacing for the minimal energy (static HF equilibrium) is lower than expected. However whether the indirect crossing (blue-green) supports the equilibrium location of the reference and indeed is a general feature of the equilibria cannot be concluded from this calculation only.

Macroscopic trends for all chiralities It has been demonstrated by means of both theoretical models, such as the tight binding model, and by concrete enumerations of the atomistic Hartree-Fock equations that the size of the band gap is very sensitive to not only to the lattice vector but also to the chirality of the nanotube. Those two parameters are substantially different because lattice spacing can be continuously shrunk while the helicity can only be changed discretely. Moreover, as explored in the section about the elastic properties, an infinitesimal change in the lattice spacing requires infinitesimal energy difference. This is not true for chiralities and in fact for a change of chirality many bonds would have to break. True enough it has been observed that a single bond can be modified, as in the case of Stone-Walse defect, but it would not happen for macroscopic number of bonds. Therefore it is much more of a robust parameter to describe the system. Nevertheless, before going into how bandgap depends on the chirality, it would be interesting to observe a macroscopic relationship how on average the bandgap changes with the diameter of the nanotube. This is to a great extent motivated by experimental constrains, as the diameter of the nanotube is one of the very few observables that can be measured, by means of a tunneling microscope.

Now, there are only two ways to increase the diameter of the nanotube if the crystal symmetries are to be kept intact. First by modifying the lattice spacing, secondly by changing the chiral vector. The case changing the lattice spacing was explored in the section above, here the focus is put on the change arising from the helicity of the nanotubes. Mind you, that to be totally rigorous, for each helicity of the tube the geometry should be optimised to find the equilibrium separation. Then the band structure should be calculated for that geometry only, and from there the values of the bandgaps should be extracted. This would be a fairly involved task, though quite easily done. Instead here it is assumed that the equilibrium separation for a given nanotube depends just slightly from that of the graphene. It is also assumed that those two separations are close enough that in the process of changing the separation to the equilibrium one, no abrupt changes of band structure would happen. Therefore the values of bandgaps would be shifted just slightly if the optimal geometries would be considered instead.

A general trend that should be observed is that the system recovers some properties of the graphene for large chiralities because locally the structure of graphene is identical to the one of the large diameter nanotube. The magnitude of the chirality vector describes the circumference of the nanotube, which is linearly proportional to the diameter. A second general statement is that the bandstructure depends significantly on the direction of the chirality vector rather than on the magnitude of it. Therefore the same diameter several distinct bandgaps exist. Now it is also clear that as the diameter is increased more possibilities appear to construct the chiral vector of certain size on the graphene sheet. Therefore it is expected that in the left plot of 3.3 the points will be more densely packed as the radius increases. It can also be observed that the bandgaps belong to either to the group of nearly zero or to the semiconducting group that is monotonous in shape.

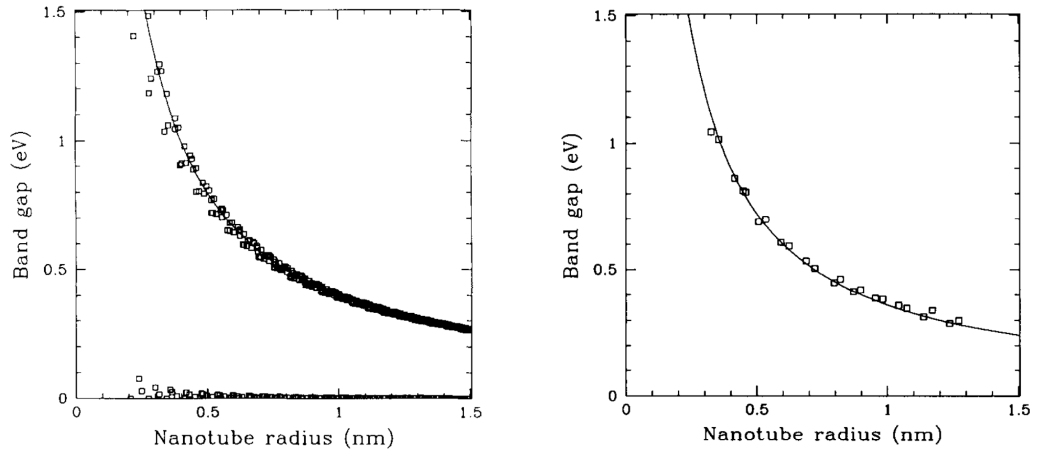


Figure 3.11: Adapted from White and Mintmire[17]

If we are to compare it to the results obtained here we don't see the metallic section. This is partly due to the Brillouin zone sampling issue presented above 3.8 and partly due to focusing on semiconducting nanotubes. Even though the bandgaps are overestimated, both basis sets recover the same monotonic increasing with decreasing radius. The fit on the values calculated by Double-Zeta is also logarithmic but doesn't converge to zero. Since for DZ basis the only reliable bandgap value is the direct in both indexes, therefore that one is used even if smaller indirect bandgap exists. On the other hand for the MINI basis the smallest bandgaps equal the smallest direct bandgap. Therefore the fit on the values obtained by MINI basis is more promising as it converges to smaller values as the lower ones have not been traced out. It is important to state that the red points of the graph converged to a lower total energy and therefore are more stable reference points. For this reason the fit preferred the red points.

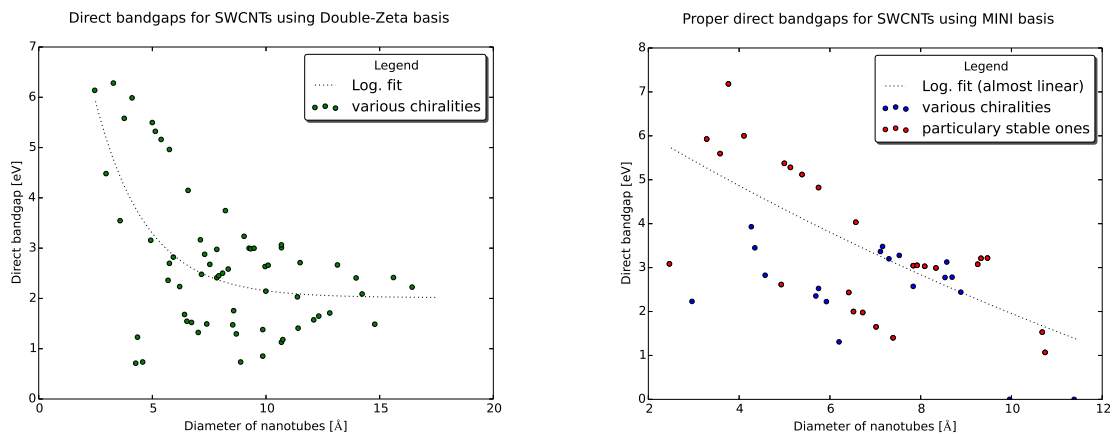


Figure 3.12: Direct bandgaps calculated with DZ (left) and MINI(right) basis.

For the sake of completeness consider the full spectrum all of which still consistent in bandgaps but with only slightly higher energy

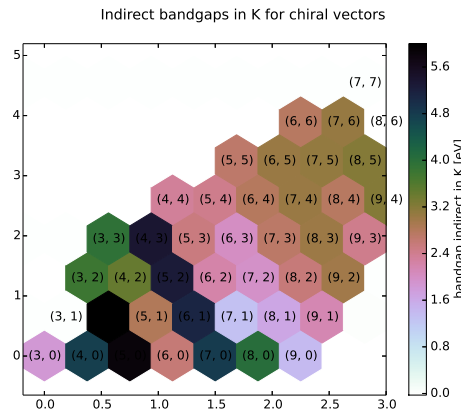


Figure 3.14: The values are the same as above but the colour scale is adjusted

address the full set.

It is true that generally the bandgaps are overestimated and this can be seen in comparison with the other methods, either simple theoretical models, or DFT. What remains true is also that the theoretical models should serve mainly as guidelines as they are unable to precisely accommodate the many body effects not even at the Hartree-Fock level. Of course the models exist that are able to describe certain trends but the particular form of those is imposed by design and the peculiarities of intensity are fine tuned by constants. Numerical techniques on the other hand, even those that like to refer to themselves to as ab initio, for instance DFT, posses a degree of freedom by which a range of results can be obtained. This is pointing to the definition of the underlying functional which usually constitutes of the exchange term and the LDA term that are free to be mixed as the physics requires. Of it makes sense to fine tune it in accord with the benchmarks, either experimental or ones obtained by more advanced methods such as the coupled cluster, a golden standard for small to medium molecules. But the difficulty is that no measurements are able conclusively identify the particular chirality of the nanotube and so possible results of both the raman spectra and the electronic spectroscopy cannot be linked to particular chiralities with certainty. Therefore the question then arises; to what are supposed to refer calculations that are to be benchmarks.

The answer is that they are supposed to refer to nothing else than few fundamental constants such as $\hbar, \epsilon, q_e, \pi$ and are supposed to be continuously improvable without any further degree of freedom. The method presented here is of this kind.

for the performance of the of the other basis set refer to the appendix below.

4 Summary and further outlook

Summary of the method: It is a known fact that at the HF level the bandgaps are usually overestimated, which has been observed in the previous sections, too. This happened even for structures that were predicted to behave as metals. The main reason is that the treatment of the electron correlation at this level is by far not complete. Even though the lacking energy contributions account just for about 1% of the total energy, impact of the electron correlation on properties is much more pronounced. In spite of the fact that density functional based methods often provide satisfactory results, at present there does not exist a systematic hierarchy towards an exact answer. In wave function approaches such hierarchies are at hand, though the formal computational complexity increases too rapidly with higher and higher level of accuracy. Hence for extended systems we are interested in, we are forced to remain at lower levels, or at least approximations that would be computationally tractable. Such a hierarchy is provided within the Coupled Cluster Theory which we shall outline below.

There is, however, a second aspect that has not been mentioned in this work. Namely, that we have implicitly worked with the non-relativistic Hamiltonian and the Born-Oppenheimer approximation was assumed. In such a model e. g. spin-orbit or electron-phonon couplings are missing. For those reasons the appendix includes brief description and comments on possible inclusion of these effects.

4.1 The Coupled Cluster Theory

Within the HF (Roothan) solution we obtain a set of orbitals whose number is (as a rule) higher than the number of spin-orbitals that are used to build the Slater determinant in the HF theory, i. e. those occupied by the electrons. Let us denote such a determinant as the reference one $|\Phi\rangle$. The orbitals that are not used in $|\Phi\rangle$ are referred to as virtual. If we define an operator $\hat{T}_n$ which replaces n spin-orbitals in $|\Phi\rangle$ by n virtual orbitals, we speak about an n -particle excitation operator. If we denote by i, j, k, l the occupied orbitals and by a, b, c, d the virtual orbitals then we can more explicitly

$$\hat{T}_1 = \sum_{i,a} t_a^i \tilde{a}_i^a \quad (4.1)$$

$$\hat{T}_2 = \frac{1}{2} \sum_{i,j,a,b} t_{ab}^{ij} \tilde{a}_{ij}^{ab} \quad (4.2)$$

$$\hat{T}_n = \frac{1}{n!} \sum_{i_1 \dots i_n, a_1 \dots a_n} t_{a_1 \dots a_n}^{i_1 \dots i_n} \tilde{a}_{i_1 \dots i_n}^{a_1 \dots a_n} \quad (4.3)$$

where $\tilde{a}$ are the true n -particle excitation operators creating the pertinent excited determinants and t are related scalar amplitudes, i. e. weights of those determinants in the final wave function expansion. Let us assume (and this is in HF so) that outset of spin-orbitals is orthogonal from which follows that the many-particle basis of (excited) Slater determinants is orthogonal, too. A multiple action of excitation operators is also possible that leads either to cumulatively excited determinants or zero when the excitation is not possible.

We can define a global excitation operator:

$$\hat{T} = \sum_n \hat{T}_n. \quad (4.4)$$

For the given one particle orbital basis the exact wave function $|\Psi\rangle$ can be expressed in the well known configuration state function expansion as

$$|\Psi\rangle = \sum_n \hat{T}_n |\Phi\rangle = \hat{T} |\Phi\rangle. \quad (4.5)$$

The development and experience during the last fifty years proved that the cluster expansion of $|\Psi\rangle$ that takes form

$$|\Psi\rangle = e^{\hat{T}} |\Phi\rangle \quad (4.6)$$

is a better alternative [?], mainly because it preserves size-extensivity when the $\hat{T}$ operator is truncated, and important higher excitations are factorized as products of $\hat{T}_n$ s. Clearly, because of the orthogonality of the determinats we have an intermediate normalization>

$$\langle\Phi||\Psi\rangle = 1 \quad (4.7)$$

The origins of coupled cluster methods trace back to the fifties, when the community of nuclear physicists believed that it should be possible to solve the many body nuclear problem by numerical means. The motivation for this stemmed also from the newly available nucleon scattering experiments that yielded the two-body forces. However, unlike in the molecular problem, there is no defining central field (analogous to Coulomb's) for the independent particle description of nucleons. The analysis of experimentally measured phases suggested several distinct forms of internucleon potentials. However, all of them possessed long range attractive tails, due to the pion exchange, and short range repulsive “hard core” potential (almost infinite in magnitude) due to the exchange of heavier mesons. This made the mean field description unfeasible due to almost infinite elements of the potential operator. Fortunately Bruckner[25] managed to describe the problem in simple plane wave basis set and express the correlation energy by means of a sum of ladder diagrams. The amplitudes were described by “Bethe-Goldstone” equations. At last the linked cluster theorem was proven by Goldstone. Shortly afterwards it became clear that the expansion naturally demonstrated the exponential structure [26, 27]. A practical tool to derive the pertinent equations to determine the amplitudes of $\hat{T}$ for many fermion systems was published fifty years ago by Čížek [28, 29], which has been a breakthrough towards massive quantum chemical usage. Čížek also showed that if $\hat{T}$ includes all possible excitations expansion (4.5) and (4.6) are fully equivalent.

Irrespective of (by far) non-trivial technicalities, the $\hat{T}$ amplitudes are obtained very simply. We have to solve the Schrödinger equation

$$\hat{H} e^{\hat{T}} |\Phi\rangle = E e^{\hat{T}} |\Phi\rangle \quad (4.8)$$

which we multiply from the left by $e^{-\hat{T}}$ and project onto various excited Slater determinats.

Let us introduce an effective Hamiltonian

$$\bar{H} = e^{-\hat{T}} \hat{H} e^{\hat{T}}. \quad (4.9)$$

It turns out that this seemingly infinite expansion effectively terminates after the fourth power of $\hat{T}$ at worst [?].

Now we can write

$$E = \langle \Phi | \bar{H} | \Phi \rangle \quad (4.10)$$

$$0 = \langle \Phi_n | \bar{H} | \Phi, \rangle \quad (4.11)$$

where Eqs (4.11) serve to determine the amplitudes of $\hat{T}_n$.

The reference determinant does not need to be a Hartree-Fock determinant. In fact, as recently Noga and Šimunek showed [30, 31], starting from an arbitrary reference and using the ansatz with $\hat{T} = \hat{T}_1$ gives rise to very efficient alternative Hartree-Fock solution without diagonalizations. Implementation of such an approach is our next goal. The great advantage would be $\hat{T}_1$ in the $\mathbf{k}$ -space factorizes single-excitation in individual $\mathbf{k}$ -points, i. e. one would work with $\hat{T}_1^{(\mathbf{k})}$ operators that involve $n_o^{(\mathbf{k})} n_v^{(\mathbf{k})}$ amplitudes, where $n_o^{(\mathbf{k})}$ and $n_v^{(\mathbf{k})}$ are numbers of occupied and virtual orbitals for the given $\mathbf{k}$ -point, respectively. This is even smaller number of parameters than for $\mathbf{c}^{\mathbf{k}}$ in the Roothan equation.

Perturbation expansion

Let us now use the perturbation expansion with the coupled cluster ansatz for the wave function.

Now one treats the Hamiltonian as consisting of the part $\hat{H}_0$ for which we now the solution and a perturbation $\hat{V}$ comming with an arbitrary parameter λ

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \quad (4.12)$$

The energy functional with the ansatz (4.6) reads:

$$\mathcal{E}(\hat{T}^\dagger, \hat{T}) = \frac{\langle \Phi | e^{\hat{T}^\dagger} (\hat{H}_0 + \lambda \hat{V}) e^{\hat{T}} | \Phi \rangle}{\langle \Phi | e^{\hat{T}^\dagger} e^{\hat{T}} | \Phi \rangle} = \langle \Phi | \left(e^{\hat{T}^\dagger} (\hat{H}_0 + \lambda \hat{V}) e^{\hat{T}} \right)_C | \Phi \rangle \quad (4.13)$$

where index "C" means connected terms [29]. Now (4.13) formally represents an infinite number of terms, but we can expand the energy (4.13) and the cluster operator in a power series of λ :

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} + \lambda^2 \mathcal{E}^{(2)} + \dots \quad (4.14)$$

$$\hat{T} = \hat{T}^{(0)} + \lambda \hat{T}^{(1)} + \lambda^2 \hat{T}^{(2)} + \dots \quad (4.15)$$

and truncate this series order by order in powers of λ . If $\hat{H}_0$ is the sum of Fock operators for all particles (electrons) in the system then we speak about Møller-Plesset (MP) partitioning of the Hamiltonian, and correspondingly about Møller-Plesset perturbation theory [?]. Then

$$E_{HF} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} = \langle \Phi | \hat{H}_0 + \hat{V}_0 | \Phi \rangle \quad (4.16)$$

and the second order functional reads:

$$\mathcal{E}^{\{2\}} = \langle \Phi | [\hat{T}^{(1)\dagger} \hat{V} + \hat{V} \hat{T}^{(1)} + \hat{T}^{(1)\dagger} \hat{H}_0 \hat{T}^{(1)}]_C | \Phi \rangle, \quad (4.17)$$

Its differentiation w.r.t. the amplitudes of $\hat{T}^\dagger$ provides the stationarity condition

$$\langle \Phi_{ij}^{ab} | (\hat{V} + \hat{H}_0) \hat{T}^{(1)} | \Phi \rangle = 0 \quad (4.18)$$

inherent to MP2 theory, from which the $\hat{T}$ amplitudes are obtained, and we observe that $\hat{T} = \hat{T}_2$, i. e. only doubly excited configurations are involved. The second order energy is then easily obtained as:

$$E^{(2)} = \langle \Phi | \hat{V} \hat{T}^{(1)} | \Phi \rangle \quad (4.19)$$

MÅzller-Plesset perturbation theory to second order represents the simplest wavefunction approach to account for the electronic correlation. The improvement of the Hartree-Fock reference energy by MP2 is significant as manifested by benchmarks of dispersion interaction, barrier heights and equilibrium geometries. In conventional basis the MP2 scales as $O(N^5)$ where N is proportional to system size. This scaling is still very demanding in order to be used in extended systems. Recently, it has been demonstrated [32] that even if the $\hat{T}$ operator in (4.6) is restricted to special double-excitations of doubly occupied singlet pairs i. e.

$$\hat{T} = \hat{T}_p = \sum_{i,a} T_a^i \tilde{a}_{i\uparrow i\downarrow}^{a\uparrow a\downarrow}, \quad (4.20)$$

the wave function fairly well treats the strong electron correlation. Using such an approach in MP2 combined with an optimized Thouless expansion as done in Ref. [33] would give rise to a method feasible for extended systems such as we use for the nanotubes. In Eq. (4.20) double excitation amplitude T_i^a formally corresponds to the same dimension of single excitations, though, now a and i can be from different $\mathbf{k}$ -points. Nevertheless, the algorithm could be adopted to $O(N^3)$ scaling, not exceeding the demands for HF.

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Appendix A Alternative derivation

The solutions of the energy levels for a periodic system can be approached by solving Schrodinger equation for one electron in an effective potential $V(r)$

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right] \psi_{\mathbf{k}}(\mathbf{r}) = E_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}), \quad (\text{A.1})$$

where m stands for electron mass, $\psi_{\mathbf{k}}(r)$ and $E_{\mathbf{k}}$ are one particle eigenfunctions and energy eigenvalues for particular wavevector k . In this scheme the interactions among electrons and between electrons and nuclei are considered by means of the effective potential $V(r) = V_{ion}(r) + V_{el}(r)$. The assumption is that electrons feel the presence of ions and other electrons only through the spin-independent potentials $V_{ion}(r)$ and $V_{el}(r)$ that are periodic under lattice translations. The generalised Tight Binding model, referred to as Linear Combination of Atomic Orbitals (LCAO), is based on the premise that the one electron wavefunction $\psi_{\mathbf{k}}(\mathbf{r})$, for all wavevectors k , can be built from basis states $\varphi_{\mathbf{k}\mathbf{r}}(\mathbf{r})$. For instance, a basis formed from eigenstates (orbitals) of hydrogen atom would be suitable as the orbitals are orthogonal* and form a complete set of functions** over $\mathbb{R}^3$ inherited from spherical harmonics constructed by Legendre polynomials [14][34].

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_a c_{\mathbf{k}a} \varphi_{\mathbf{k}\mathbf{r}}(\mathbf{r}) \quad (\text{A.2})$$

The tensor $c_{\mathbf{k}a}$, of a rank of the dimensionality of $\mathbf{k}$, represents the expansion coefficients of $\psi_{\mathbf{k}}(\mathbf{r})$ in terms of the basis $\varphi_{\mathbf{k}\mathbf{r}}(\mathbf{r})$. The requirement of the wavefunction to be periodic under translation makes it convenient to use basis that a priori satisfies Bloch's condition.

$$\varphi_{\mathbf{k}a}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i\mathbf{k} \cdot \mathbf{R}(\mathbf{l})} \chi_a(\mathbf{R}(\mathbf{l}) - \mathbf{r}) \quad (\text{A.3})$$

Where χ_a are the basis functions localised at $R(l)$, a position vector of the atom in the l^{th} unit cell, N is the number of unit cells considered. [35] In practice it is wise to choose Gaussians as the local basis set basis χ_a for the ease of integral evaluation as opposed to atomic basis set.

For graphene the two lattice parameters are equal $R(l) = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 = \mathbf{l}a$ and so one can introduce a dimensionless wavevector $\mathbf{k} = \begin{pmatrix} k_1 \\ k_2 \end{pmatrix}$ and rewrite the formula (3) as

$$\varphi_{\mathbf{k}a}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i\mathbf{k} \cdot \mathbf{l}} \chi_a(\mathbf{R}(\mathbf{l}) - \mathbf{r}) \quad (\text{A.4})$$

Now the problem can be solved by substituting equation (4) into (2) and then to (1). This approach also for the case of nanotubes but the number of atoms in the unit cell would be very large, particularly for chiral nanotubes. Instead one can use the same formalism with adopting for the screw symmetry on top of the translational one. This allows any nanotube to be described by a unit cell consisting of only two atoms [17]. Implementation of the former idea begins with expressing the symetrised wavefunctions that satisfy Bloch's condition under screw operations with arbitrary $\mathbf{l}$

$$\varphi_{\mathbf{k}a}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}a'} e^{i\mathbf{k}\cdot\mathbf{l}} \hat{T}_{aa'}(\mathbf{l}) \chi_{a'}(\mathbf{R}(\mathbf{l}) - \mathbf{r}) \quad (\text{A.5})$$

Here the rotation tensor $\hat{T}_{rr'}(\mathbf{l})$ is introduced that rotates the basis orbitals around the circumference of the tubulus. For symmetric orbitals χ the rotation would be irrelevant as the same basis element would be achieved by translation only. For the sake of demonstration one could imagine $\mathbf{p}$ orbitals along the naonotube that need not only to be translated to the correct atomic sites but also need to be rotated appropriately in order for the Bloch function created from them be invariant under the screw symmetry operation.

Now in solving for the eigenvalues the equation (1) includes one more index r' to sum.

$$\sum_{a'} c_{\mathbf{k}a} H_{\mathbf{k}aa'} = E_{\mathbf{k}} \sum_{a'} c_{\mathbf{k}a'} S_{\mathbf{k}aa'} \quad (\text{A.6})$$

Where the Hamiltonian H and the overlap matrix S need to be adjusted for the screw rotation for every $\mathbf{k}$ as

$$H_{\mathbf{k}aa'} = \sum_{\mathbf{l}a''} e^{i\mathbf{k}\cdot\mathbf{l}} H_{aa''}(\mathbf{l}) T_{a''a'}(\mathbf{l}) \quad (\text{A.7})$$

$$S_{\mathbf{k}aa'} = \sum_{\mathbf{l}a''} e^{i\mathbf{k}\cdot\mathbf{l}} S_{aa''}(\mathbf{l}) T_{a''a'}(\mathbf{l}) \quad (\text{A.8})$$

Where the elements of the hamiltonian $H_{aa'}(\mathbf{l})$ and the overlap matrix $S_{aa'}(\mathbf{l})$ can be expressed for atoms in the cells 0 and 1 at locations $\mathbf{R}(\mathbf{l})$ and $\mathbf{R}'(\mathbf{l})$ ($\mathbf{R}, \mathbf{R}'$ denoting two atoms in the unit cell 1)

$$H_{aa'}(\mathbf{l}) = \int d\mathbf{r} \chi_a(\mathbf{R}(\mathbf{0}) - \mathbf{r}) \hat{H} \chi_{a'}(\mathbf{R}'(\mathbf{l}) - \mathbf{r}) \quad (\text{A.9})$$

$$S_{aa'}(\mathbf{l}) = \int d\mathbf{r} \chi_a(\mathbf{R}(\mathbf{0}) - \mathbf{r}) \hat{S} \chi_{a'}(\mathbf{R}'(\mathbf{l}) - \mathbf{r}) \quad (\text{A.10})$$

Since the surface of the tube is a two dimensional manifold, so the solutions of the wavevectors need to have two independent directions. A convenient choice is that points along the direction of the tube while the other is normal to it pointing along the circumference. These are the constituents of $\mathbf{k} = \begin{pmatrix} k_1 \\ k_2 \end{pmatrix}$. The boundary conditions of the tube allow for a discrete number of possible wavevectors k_1, k_2

$$k_1 L_1 + k_2 L_2 = 2\pi l \quad (\text{A.11})$$

$$k_1 N_1 + k_2 N_2 = k \quad (\text{A.12})$$

Where k is one dimensional wavevector of the of the tube ranging from $-\pi$ to π and the integer l labels the electronic energy levels with a given k ($l = 0, 1, \dots, N_c - 1$). So we can further express the boundary conditions as

$$k_1 = \frac{(2\pi N_2 l - L_2 k)}{N_c} \quad k_2 = \frac{(L_1 k - 2\pi N_1 l)}{N_c} \quad (\text{A.13})$$

Therefore we need only to consider those k-points in creating the series of a Bloch functions with only two scalar indices k, l . Where $\mathbf{l}$ runs over the indices of the two-atom unit cells in the translational unit cell. To simplify the notation the two scalar functions with a vector argument are introduced

$$\alpha(\mathbf{l}) = \frac{2\pi(l_1 N_2 - l_2 N_1)}{N_c} \quad (\text{A.14})$$

$$z(\mathbf{l}) = \frac{(L_1 l_2 - L_2 l_1)}{N_c} \quad (\text{A.15})$$

So the Bloch functions are constructed after appropriate transformation of orientations of orbitals with the use of rotational operator $\hat{T}_{aa'}(\mathbf{l})$. This idea has been pioneered by [22]

$$\varphi_{kla}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i(\alpha(\mathbf{l})l + z(\mathbf{l})k)} \hat{T}_{aa'}(\mathbf{l}) \chi_{a'}(\mathbf{R}(\mathbf{l}) - \mathbf{r}) \quad (\text{A.16})$$

to find the coefficients $c_{kla'}$ from

$$\sum_{a'} c_{kla} H_{klaa'} = E_{kl} \sum_{a'} c_{kla'} S_{klaa'} \quad (\text{A.17})$$

$$H_{klaa'} = \sum_{\mathbf{la}''} e^{i(\alpha(\mathbf{l})l + z(\mathbf{l})k)} H_{aa''}(\mathbf{l}) T_{a''a'}(\mathbf{l}) \quad (\text{A.18})$$

$$S_{klaa'} = \sum_{\mathbf{la}''} e^{i(\alpha(\mathbf{l})l + z(\mathbf{l})k)} S_{aa''}(\mathbf{l}) T_{a''a'}(\mathbf{l}) \quad (\text{A.19})$$

Having established this set of linear algebraic equations (7) having a nontrivial solutions for coefficients $c_{kla'}$, that define the one particle eigenvectors, only for corresponding eigenvalues of energy E that satisfy the characteristic equation

$$\|H_{klaa'} - E_{kl} S_{klaa'}\| = 0 \quad (\text{A.20})$$

which in terms of linear algebra is equivalent to diagonalisation of matrix of size of H . Of course now when the eigenenergies E are found and corresponding eigenvectors c determine one body wavefunctions one can construct a many body wavefunction by the antisymmetrising the product of one body wavefunctions by means of a Slater determinant wavefunction.

and the many body wavefunction described by an antisymmetrised product

$$\Psi^{HF}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \hat{A} \prod \varphi(\mathbf{r}_i) \quad (\text{A.21})$$

then the potential term in the hamiltonian $V(r)$ is adjusted accordingly and the equation (8) is calculated until self consistency is reached by solving the secular equation.

The energy per unit cell is then the sum over the lowest eigenvalues for occupied states

$$E = \sum_{klm}^{occ} E_{klm} + \frac{1}{2} \sum_{i,j} \phi(r_{ij}) \quad (\text{A.22})$$

Appendix B Basis-Sets

In this work, orbitals of Gaussian type are employed.

$$\mu_p(\mathbf{r}) = (x - R_x)^l (y - R_y)^m (z - R_z)^n \exp \left[-\eta (\mathbf{r} - \mathbf{R} - \mathbf{p})^2 \right] \quad (\text{B.1})$$

Here the integers (l, m, n) determine the orbital angular momentum, η is the exponent of the Gaussian that determines its spread. For the vectors, $\mathbf{r} = (x, y, z)$ is where the density of the orbital is evaluated, $\mathbf{R}$ points to the centre of the orbital, in this case either of the two atoms in the unit cell, and $\mathbf{p}$ maps the particular unit cell to the origin.

! Basis = DZP (Dunning)

2	1	1	1		
	7	2			
4232.610000		0.0020290	0.0000000	0.0000000	0.0000000
634.8820000		0.0155350	0.0000000	0.0000000	0.0000000
146.0970000		0.0754110	0.0000000	0.0000000	0.0000000
42.4974000		0.2571210	0.0000000	0.0000000	0.0000000
14.1892000		0.5965550	0.0000000	0.0000000	0.0000000
1.9666000		0.2425170	0.0000000	1.0000000	0.0000000
5.1477000		0.0000000	1.0000000	0.0000000	0.0000000
4	1				
18.1557000		0.0185340	0.0000000		
3.9864000		0.1154420	0.0000000		
1.1429000		0.3862060	0.0000000		
0.3594000		0.6400890	1.0000000		
1	1				
0.7500000		1.0000000			

! Basis = MINI

2	1	1		
	6	2		
153.1722600		0.0707400		0.0000000
23.0730300		0.3953800		0.0000000
4.9232900		0.6633110		0.0000000
5.7255700		0.0000000		-0.0813800
0.4550400		0.0000000		0.5748530
0.1470700		0.0000000		0.5024130

3	1
4.2513100	0.1099310
0.8632700	0.4627130
0.2013500	0.6275140

Appendix C Table

<i>Hel.</i>	<i>Diam.</i> [$\text{\AA}$]	<i># itrs.</i>	<i>E_{tot}</i> [Ha]	<i>Dir. gap</i> [eV]	<i>Indir. k</i> [eV]	<i>Indir. K</i> [eV]	<i>Indir. K, k</i> [eV]
3 0	2.46	25	-75.03	3.086	3.086	1.860	0
4 0	3.29	26	-75.12	5.927	5.927	4.762	3.655
3 2	3.58	46	-75.18	5.596	4.484	3.801	3.609
4 1	3.76	50	-75.15	7.183	7.183	6.234	4.253
5 0	4.11	25	-75.15	5.999	5.999	5.858	3.781
6 0	4.93	28	-75.16	2.615	2.615	2.615	2.615
4 3	5.00	36	-75.17	5.374	5.374	5.374	5.374
5 2	5.13	24	-75.17	5.282	5.282	5.282	5.282
6 1	5.39	24	-75.17	5.119	5.119	5.119	5.119
7 0	5.75	24	-75.17	4.823	4.823	4.823	4.823
5 4	6.42	46	-75.18	2.435	2.435	2.435	2.435
6 3	6.52	24	-75.18	2.000	2.000	2.000	2.000
8 0	6.57	24	-75.18	4.033	4.033	4.033	4.033
7 2	6.72	25	-75.18	1.978	1.978	1.978	1.978
8 1	7.02	25	-75.18	1.651	1.651	1.651	1.651
9 0	7.39	24	-75.18	1.402	1.402	1.402	1.402
6 5	7.84	45	-75.18	3.044	3.044	3.044	3.044
7 4	7.92	46	-75.18	3.052	3.052	3.052	3.052
8 3	8.09	47	-75.19	3.030	3.030	3.030	3.030
10 0	8.21	23	-75.19	3.797	3.797	3.797	3.797
9 2	8.34	24	-75.19	2.992	2.992	2.992	2.992
11 0	9.03	23	-75.19	3.025	3.025	3.025	3.025
7 6	9.26	22	-75.19	3.077	3.077	3.077	3.077
8 5	9.33	44	-75.19	3.212	3.212	3.212	3.212
9 4	9.47	45	-75.19	3.218	3.218	3.218	3.218
12 0	9.86	23	-75.19	0.925	0.925	0.925	0.925
8 7	10.68	46	-75.19	1.530	1.530	1.530	1.530
9 6	10.74	22	-75.19	1.069	1.069	1.069	1.069

Table 1: Supercell of 17 translations, with lattice vector of $2.58\text{\AA}$ calculated with MINI basis for a threshold of 10^{-7}Hartree , ordered by ascending diameter.

Appendix D Additional diagrams

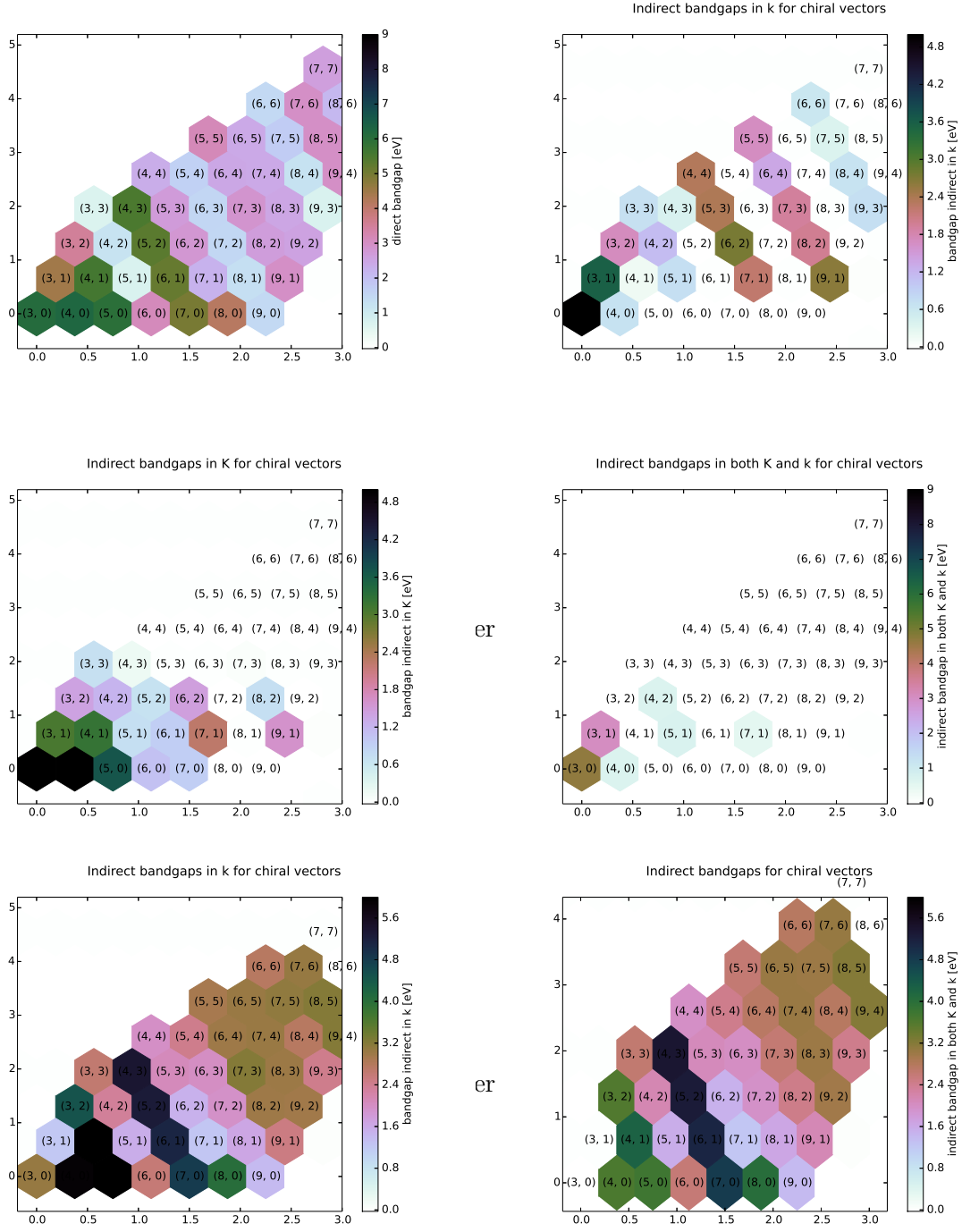


Figure D.3: indirect in k DZ

Figure D.4: indirectest DZ

Figure D.5: Total energy per cell versus lattice vector

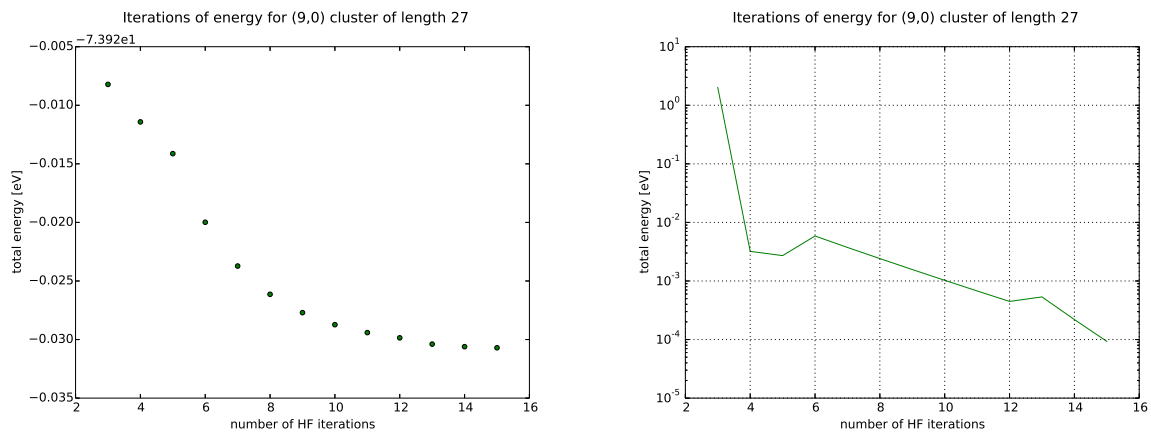


Figure D.6: Convergence properties for zig-zag nanotube

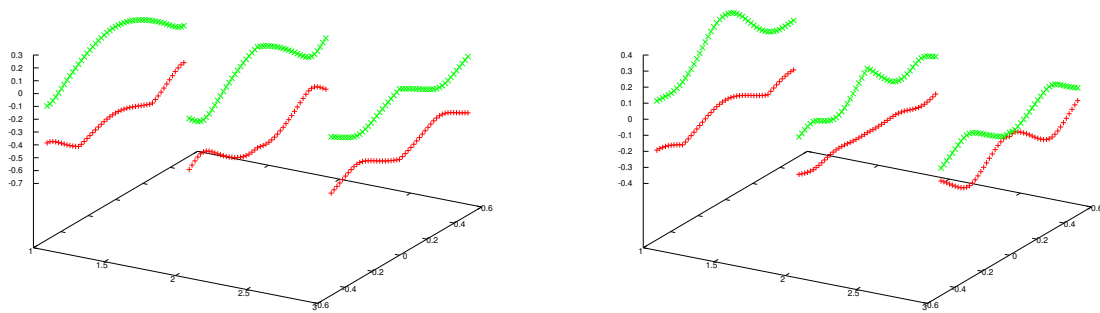


Figure D.7: **Left:** band structure for (3,2) notice Dirac points. **Right:** (5,0) mind you energy units are Hartree

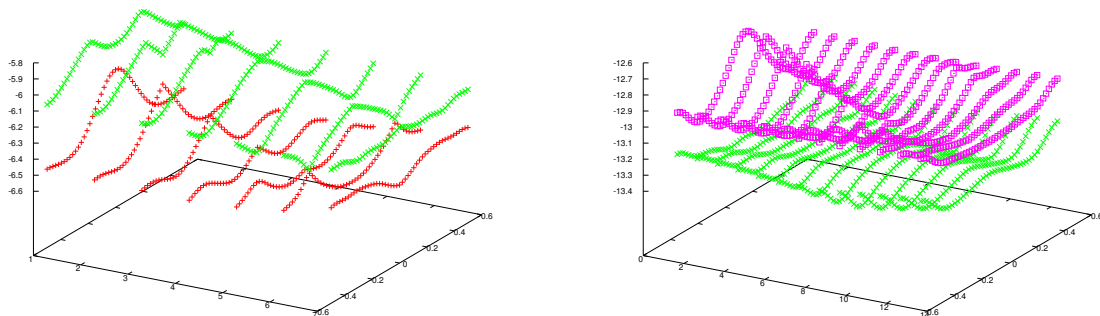


Figure D.8: **Left:** band structure for (9,3) notice Dirac points. **Right:** (12,12) mind you energy units are Hartree

Appendix E Derivations of further corrections

Electron-Phonon coupling

Once the energy gradients are enumerated and the associate phonon spectrum is calculated one is able to include further corrections as a coupling between the electronic and phonon modes. Not only it will improve the accuracy of the model, but more interestingly, it in principle is able to account for an attractive force among electrons. This in turn gives rise to remarkable behavior such as superconductivity. This derivation is adapted from the book by Bruus and Flensberg[6]. It is mentioned here for future reference in case such direction would be undertaken.

$$V_{el-ion} = \int dr (-e) \rho_{el}(r) \sum_{k=1}^N V_{ino}(r - R_j) \quad (E.1)$$

$$V_{el-ion} = \int dr (-e) \rho_{el}(r) \sum_{k=1}^N V_{ino}(r - R_j^0) - \int dr (-e) \rho_{el}(r) \sum_{k=1}^N \nabla_r V_{ino}(r - R_j^0) \cdot u_j \quad (E.2)$$

$$V_{el-ph} = \int dr \rho_{el}(r) \left\{ \sum_j e u_j \cdot \nabla_r V_{ion}(r - R_j^0) \right\} \quad (E.3)$$

$$\nabla_r V_{ion}(r - R_j^0) = \frac{1}{V} \sum_{q \in FBZ} \sum_{G \in RL} i(q + G) V_{q+G} e^{i(q+G) \cdot (r - R_j^0)} \quad (E.4)$$

$$u_j = \frac{1}{\sqrt{N}} \sum_{k \in FBZ} \sum_{\lambda} \frac{l_k}{\sqrt{2}} (b_{k\lambda} + b_{-k\lambda}^\dagger) \epsilon_{k\lambda} e^{ik \cdot R_j^0} \quad (E.5)$$

$$\sum_i e u_j \cdot \nabla_r V_{ion}(r - R_j^0) = \frac{1}{V} \sum_{\substack{q \in FBZ \\ G \in RL, \lambda}} g_{q,G,\lambda} (b_{q,\lambda} + b_{-q,\lambda}^\dagger) e^{i(q+G) \cdot r} \quad (E.6)$$

thus the phonon coupling strength $g_{q,G,\lambda}$ is introduced

$$g_{q,G,\lambda} = ie \sqrt{\frac{N\hbar}{2M\omega_{q\lambda}}} (q + G) \cdot \epsilon_{q\lambda} V_{q+G} \quad (E.7)$$

$$V_{el-ph} = \frac{1}{V} \sum_{k\sigma} \sum_{q\lambda} \sum_G g_{q,G,\lambda} c_{k+q+G}^\dagger c_{k\sigma} (b_{q\lambda} + b_{-q\lambda}^\dagger) \quad (E.8)$$

$$V_{el-ph}^{IN} = \frac{1}{V} \sum_{k\sigma} \sum_{q\lambda_l} g_{q,\lambda_l} c_{k+q,\sigma}^\dagger c_{k\sigma} (b_{q,\lambda_l} + b_{-q\lambda_l}^\dagger) \quad (E.9)$$

$$V_{el-ph}^{INA} = \frac{1}{V} \sum_{k\sigma} \sum_q g_{q,\lambda_l} c_{k+q,\sigma}^\dagger c_{k\sigma} (b_q + b_{-q}^\dagger) \quad (E.10)$$

this model considers Yukawa potential, however the numerical method has those densities at hand that can be used.

$$V_q = \frac{Ze}{\epsilon_0} \frac{1}{q^2 + k_s^2} \quad (\text{E.11})$$

therefore the coupling constant could be determined for a specific system, if this procedure would be implemented.

$$g_q = i \frac{Ze^2}{\epsilon_0} \frac{q}{q^2 + k_s^2} \sqrt{\frac{N\hbar}{2M\omega_q}} \quad (\text{E.12})$$

Basic Spin-orbit coupling

The task to enumerate the electronic behavior, by means of band structure, has several distinct bottlenecks and therefore several ways in which the description would approach the reality. The areas are Correlation effects, Size of The cluster and inclusion of spin effects. Despite the spin related effects have had only marginal influence on the result, they are very interesting from the phenomenological perspective.

So far the description of the electronic properties were limited to spin-less charge carriers. If we are to include these effects

Consider the simple Hamiltonian for single hydrogen atom introduced in I. The first term represents the energy of the atom in the centre of mass frame, with μ being the reduced mass of proton and electron.

$$H_0 = \frac{\hat{\mathbf{P}}^2}{2\mu} + V(R) \quad (\text{E.13})$$

The second term represents the electrostatic interaction energy between the proton and the electron of charge q .

$$V(R) = -\frac{q^2}{4\pi\epsilon_0} \frac{1}{R} = -\frac{e^2}{R} \quad (\text{E.14})$$

The former Hamiltonian was referred to as simple due to its negligence relativistic effects, and magnetic interactions arising from spin of both particles. One could argue that the magnetic moment of the nucleus is very small and so the associated effects are insignificant. Likewise for the hydrogen's mass and so energy being also very small the relativistic effects caused by the distortion of the spacetime in the vicinity of the nucleus are marginal. In fact this simple Hamiltonian has proven to be consistent with experimentally measured spectral lines and rightly so stands its ground.

A detailed study of particular lines reveals the splitting of energy levels that cannot be explained without the aforementioned fine effects. It is recognized that Dirac equation satisfies postulates of both quantum mechanics and special relativity and can be solved analytically for the problem of hydrogen^[1]. However this is not possible for the systems of multiple electrons and so perturbative approach is used instead. For the sake of demonstration the hamiltonian of hydrogen is expanded in $\frac{c}{v}$ of the correction term W

$$H = m_e c^2 + H_0 - \frac{\mathbf{P}^4}{8m_e^3 c^2} + \frac{1}{2m_e^2 c^2 R} \frac{dV(R)}{dR} \mathbf{L} \cdot \mathbf{S} + \frac{\hbar^2}{8m_e^3 c^2} \Delta V(R) + \dots \quad (\text{E.15})$$

Rayleigh-Schrodinger Perturbative scheme

$$\hat{H}\Psi_n = E_n\Psi_n \quad (\text{E.16})$$

$$\hat{H} = \hat{H}_0 + \lambda\hat{V} \quad (\text{E.17})$$

$$\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \quad (\text{E.18})$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \quad (\text{E.19})$$

$$\Psi_n = \Psi_n^{(0)} + \lambda\Psi_n^{(1)} + \lambda^2\Psi_n^{(2)} + \dots \quad (\text{E.20})$$

$$E_n^{(k)} = \frac{1}{k!} \frac{d^k E_n}{d\lambda^k} \quad (\text{E.21})$$

$$\Psi_n^{(k)} = \frac{1}{k!} \frac{\partial^k \Psi_n}{\partial \lambda^k} \quad (\text{E.22})$$

$$\langle \Psi_n^{(0)} | \Psi_n^{(m)} \rangle = \delta_{m0} \quad (\text{E.23})$$

$$\langle \Psi_n^{(0)} | \Psi_n \rangle = 1 \quad (\text{E.24})$$

$$\hat{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \quad (\text{E.25})$$

$$\hat{H}_0\Psi_n^{(1)} + \hat{V}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_n^{(0)} \quad (\text{E.26})$$

$$\hat{H}_0\Psi_n^{(2)} + \hat{V}\Psi_n^{(1)} = E_n^{(0)}\Psi_n^{(2)} + E_n^{(1)}\Psi_n^{(1)} + E_n^{(2)}\Psi_n^{(0)} \quad (\text{E.27})$$

$$\hat{H}_0\Psi_n^{(3)} + \hat{V}\Psi_n^{(2)} = E_n^{(0)}\Psi_n^{(3)} + E_n^{(1)}\Psi_n^{(2)} + E_n^{(2)}\Psi_n^{(1)} + E_n^{(3)}\Psi_n^{(0)} \quad (\text{E.28})$$

for an orthonormal basis, the contributions separate

$$E_n^{(0)} = \langle \Psi_n^{(0)} | \hat{H}_0 | \Psi_n^{(0)} \rangle \quad (\text{E.29})$$

$$E_n^{(1)} = \langle \Psi_n^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle \quad (\text{E.30})$$

$$\vdots \quad (\text{E.31})$$

$$E_n^{(m)} = \langle \Psi_n^{(0)} | \hat{V} | \Psi_n^{(m-1)} \rangle \quad (\text{E.32})$$

$$\Psi_n^{(m)} = \sum_l C_{n,l}^{(m)} \Psi_l^{(0)} \quad (\text{E.33})$$

$$C_{n,l}^{(m)} = \langle \Psi_l^{(0)} | \Psi_n^{(m)} \rangle \quad (\text{E.34})$$

$$(E_n^{(0)} - E_l^{(0)}) \langle \Psi_l^{(0)} | \Psi_n^{(1)} \rangle = \langle \Psi_l^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle \quad (\text{E.35})$$

$$C_{n,l}^{(1)} = \frac{\langle \Psi_l^{(0)} | \hat{V} | \Psi_n^{(0)} \rangle}{(E_n^{(0)} - E_l^{(0)})} \quad (\text{E.36})$$

Møller–Plesset

In order to capture some behavior of the correlations among the electrons of the crystal one has to use methods beyond Hartree Fock that does not explicitly consider the relative positions of the electrons. The most natural method to express the improve on the accuracy and include the correlations is by means of Configuration Interaction(CI). Unlike in HF, here the many-body state is expressed not as a single slater determinant but as a linear combination of slater determinants that can be constructed from given the number electrons and orbitals, which is equivalent to number of basis elements. Of course the full configuration interaction would consider a combination of all possible slater determinants. However the number of such configuration state functions ,or slater determinants, scales exponentially with the system size so it is not feasible approach not even for molecular systems of several electrons.

The most reliable method, referred to as Coupled Cluster, is still computationally expensive. It is based on the defining work of Thaulless in nuclear physics. It is takes the exponential ansatz by which one is able to express the state function as series.. and

Møller-Plesset perturbation to second order (MP2) represents the simplest wavefunction approach to account for the electronic correlation. The improvement of the Hartree-Fock reference energy by MP2 is significant as manifested by benchmarks of dispersion interaction, barrier heights and equilibrium geometries. In conventional basis the MP2 scales as $O(N^5)$ where N is proportional to system size.

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \quad (\text{E.37})$$

$$\hat{H}_0 = \sum_i f(i) = \sum_i h(i) + V^{HF}(i) \quad (\text{E.38})$$

$$\hat{V} = \sum_{i < j} (r_{ij}^{-1} - V^{HF}) \quad (\text{E.39})$$

$$V_{pq}^{HF} = \sum_b \langle pb | qb \rangle \quad (\text{E.40})$$

$$E_0^{(1)} = \left\langle \Psi_0^{(0)} \left| \frac{1}{r_{12}} - \hat{V}^{HF} \right| \Psi_0^{(0)} \right\rangle \quad (\text{E.41})$$

$$E_n = E_n^{(0)} + E_n^{(1)} = \sum_a \epsilon_a - \frac{1}{2} \sum_{ab} \langle ab | ab \rangle \quad (\text{E.42})$$

$$\Psi_n^{(1)} = \sum_{\substack{a > b \\ r > s}} C_{n,abrs}^{(1)} \Psi_{ab}^{rs} \quad (\text{E.43})$$

$$C_{n,abrs}^{(1)} = \langle \Psi_{ab}^{rs} | \Psi_n^{(1)} \rangle = \sum_{\substack{a > b \\ r > s}} \frac{\left| \langle \Psi_{ab}^{rs} | \frac{1}{r_{12}} | \Psi_0^{(0)} \rangle \right|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (\text{E.44})$$

$$E_0^{(2)} = \sum_{\substack{a > b \\ r > s}} \frac{\left| \langle \Psi_{ab}^{rs} | \frac{1}{r_{12}} | \Psi_0^{(0)} \rangle \right|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (\text{E.45})$$

$$E_0^{(2)} = \sum_{\substack{a > b \\ r > s}} \frac{|\langle ab | rs \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (\text{E.46})$$

$$E_0^{(2)} = \frac{1}{4} \sum_{abrs} \frac{|\langle ab | rs \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (\text{E.47})$$

N electron system

$$E_0^{(2)} = 2 \sum_{abrs}^{\frac{N}{2}} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} - \sum_{abrs}^{\frac{N}{2}} \frac{\langle ab | rs \rangle \langle rs | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (\text{E.48})$$