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Nanocrystalline Nanowires: III. Electrons

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ABSTRACT

Nanocrystalline nanowires (NCNW) are fragments of bulk crystals that are infinite in only one direction and typically have some rotational symmetry around this direction. Electron eigenstates belonging to the symmetry labels (*k*,*m*) (wavevector and rotational quantum number) are discussed. The rotational quantum number simplifies discussion of optical properties. For $m \neq 0$, the $\pm m$ degeneracy allows orbital magnetism. The simplest sensible model which is more complex than a one-dimensional chain is solved. Methods are suggested for incorporating rotational symmetry into preexisting codes with three-dimensional translations.

In a 3-D crystal, the translation operators commute among themselves and with the Hamiltonian, but none of the point symmetry operators commute with all translations. Therefore, except at special k points, the eigenstates, having been labeled by the eigenvalue label $\vec{k}$ of translations, can acquire no further symmetry labels from rotations, and no further reduction of the secular equations can occur. In a nanocrystalline nanowire, translation symmetry is only along the z-axis. A nanowire may also have some rotational symmetry, by angles $2\pi/\rho$, around the z-axis. These rotations (both simple and screw rotations) commute among themselves and with the z translations. Therefore, eigenstates of operators like the Hamiltonian can be chosen to be simultaneous eigenstates of both translations and rotations. The rotational quantum number m joins the k-label for z-translations in labeling eigenstates and providing selection rules. This relatively obvious observation has been made and used before,[1] but less often than one would expect, possibly because it has been hard to disentangle from more complex symmetry considerations needed in carbon nanotubes.[2−4]

This paper follows two others about nanocrystalline nanowires.[5,6] Paper I[5] speculates about structure, and paper II[6] is about vibrational eigenstates, specifically methods and benefits of labeling them with m as well as k. The present paper extends this to electronic single-particle eigenstates. Well tested and documented electronic structure codes, developed for 3-D crystals, are often used for nanowires by the simple expedient of making virtual parallel copies of the wire, periodically, in the directions transverse to the wire, separated far enough that they do not interact. This separation implies that the wavevector components k_x, k_y, perpendicular to the wire, encode irrelevant information about phases of states on adjacent noninteracting wires. Setting $k_x = k_y = 0$ is normal, but rotational symmetry is not yet regained. One purpose of this note is to show that the modification of existing codes, needed to exploit rotations, is not very large, may be worth implementing to save time in matrix diagonalization, and is definitely worth adding after diagonalization to enable symmetry-related properties to be more easily seen and discussed.

It is useful to start with a formal observation. If the Hamiltonian matrix H is expressed in an orthonormal basis of states $|p\rangle$, then there exists a unitary transformation U, depending only on the basis set and on symmetry, such that the transformed matrix $H' = UHU^{+}$ is block-diagonal. The different blocks are labeled by different values of the quantum numbers (k,m), where $\exp(ikc)$ is the eigenvalue of translation by c along z, and $\exp(im\varphi)$ is the eigenvalue of rotation by $\varphi = 2\pi/\rho$ around z. The states $|p\rangle$ may be local functions or extended functions like plane waves. First, consider local functions. The rotation U in basis function space transforms the basis to a set of orthonormal symmetrized functions $|kmp\rangle$. The transformation is

$$|kmp\rangle = \frac{1}{\sqrt{N\rho}} \sum_{L} \sum_{\lambda=0}^{\rho-1} e^{ikl} e^{im\lambda\phi} T^{L} R^{\lambda} |p\rangle \qquad (1)$$

where $|p\rangle$ is localized on layer $l = 0$. After L z-translations by c, and λ rotations by $\varphi = 2\pi/\rho$, the site of $T^{L}R^{\lambda}|p\rangle$ has

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been raised by l layers. The unitary rotation matrix is

$$U = \sum_{kmp} |kmp\rangle\langle kmp|p\rangle\langle p| = \sum_{km} U(km) \tag{2}$$

The different rows of U belong to particular choices of (km). For each (km), there are multiple orthogonal rows, which are grouped by (km) such that U has a layered structure, a block of rows designated $U(km)$ for each (km). The submatrices $U(km)$ are not square, but can be filled up to square if convenient by adding rows of zeros. The Hamiltonian blocks can be labeled $H'(km)$ and come from the original Hamiltonian by

$$H'(km) = U(km)HU^{+}(km) \tag{3}$$

The off-diagonal submatrices $U(k'm')HU^{+}(km)$ vanish unless $k = k'$ and $m = m'$.

Once the eigenstates Ψ' of this new matrix H' are found, the eigenstates $\Psi = U^{+}\Psi'$ of H are available. The unitary matrix U is easy to construct. If $|p\rangle$ is a state localized on an atom in layer z_p and in angular sector φ_p, its matrix elements are

$$\langle kmp|p\rangle = (N\rho)^{-1/2}\, e^{-ikz_p}\, e^{-im\phi_p} \tag{4}$$

If $|p\rangle$ is a plane wave, then it is already an eigenstate of the z translation, so the transformation, while simpler, requires careful discussion, which will be given soon.

The ideas are most easily explained by reference to an example. Consider the hcp lattice, as is found, for example, in the hcp crystal structure of elements like Zn and also in the wurtzite crystal structure of binaries like ZnO. A minimal fragment of this lattice is shown in Figure 1. The lattice sites of the bulk crystal are $R_\ell = \ell_1\vec{a}_1 + \ell_2\vec{a}_2 + \ell_3\vec{a}_3$, with $\ell = (\ell_1,\ell_2,\ell_3)$ a trio of integers. The primitive lattice translations are

$$\begin{aligned} \vec{a}_1 &= a(1/2,-\sqrt{3}/2,0) \\ \vec{a}_2 &= a(1/2,+\sqrt{3}/2,0) \\ \vec{a}_3 &= c(0,0,1) \end{aligned} \tag{5}$$

The atoms of the crystal are at sites $\vec{R}_\ell + \vec{\tau}_i$, where the first atom position $\vec{\tau}_1$ is arbitrary and $\vec{\tau}_2 - \vec{\tau}_1 = (1/3)\vec{a}_1 + (2/3)\vec{a}_2 + (1/2)\vec{a}_3$. The hcp structure has two identical atoms at these two sites, while wurtzite has two additional atoms of opposite charge at positions displaced by uc in the z-direction, with $u \approx 3c/8$. The nanowire is infinite in the z direction (c-axis) but terminates in the x and y directions. A perfect nanocrystalline nanowire has perfect translational symmetry in the z-direction. The $x-y$ plane termination is independent of z. Let us assume some rotational symmetry around the growth axis. For hcp structure, the rotational symmetry can be a 3-fold simple axis, if the symmetry axis is chosen through an atom ($\vec{\tau}_1 = 0$), a 2-fold screw axis, if the symmetry axis is chosen halfway between atoms ($\vec{\tau}_1 = -\vec{\tau}_2$), or a 6-fold screw axis, if the axis of symmetry passes through vacant hexagonal sites ($\vec{\tau}_1 = (1/3)\vec{a}_1 + (2/3)\vec{a}_2$). The 6-fold case is shown in Figure 1, which also shows some symmetrized local basis functions.

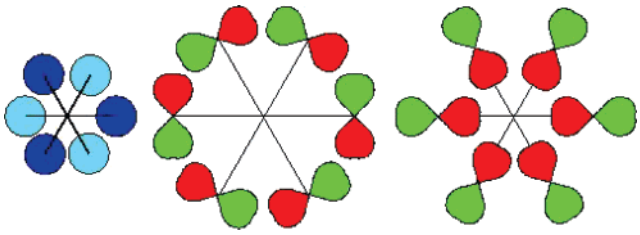

Figure 1. On the left are the six identical atoms of the primitive translational unit of the smallest 6-fold nanorod. Pale blue represents atoms stacked at $z = c/2$ relative to the dark blue atoms at $z = 0$. One can also imagine the dark and pale blue to represent s orbitals on the 6 basis atoms, with alternating signs arising either from having $k = 0$ and $m = 3$, or alternately, $m = 0$ and $k = \pi/c$. The middle and right panels show symmetrized combinations of p_x and p_y orbitals, arranged to be eigenstates of rotation with $m = 0$.

Suppose the orthogonal basis is plane waves. The translational unit has height c in the z-direction, but in the transverse directions, the distance is the artificial superlattice separation of the parallel lattice of nanowires. If the superlattice translations are multiples of the hcp lattice translations, $\vec{R}_1 = F\vec{a}_1$, $\vec{R}_2 = F\vec{a}_2$, then the rotational symmetry of the nanowire is preserved in the superlattice. The distance Fa should be larger than the nanowire radius by at a minimum separation of 5−10 Å. The reciprocal lattice vectors are then $\vec{G}_n = n_1\vec{G}_1 + n_2\vec{G}_2 + n_3\vec{G}_3$ and

$$\begin{aligned} \vec{G}_1 &= (2\pi/Fa)(2/\sqrt{3})(\sqrt{3}/2,-1/2,0) \\ \vec{G}_2 &= (2\pi/Fa)(2/\sqrt{3})(\sqrt{3}/2,+1/2,0) \\ \vec{G}_1 &= (2\pi/c)(0,0,1) \end{aligned} \tag{6}$$

The Bloch states of the superlattice are $|\vec{k}_j\rangle = \sum_G A_j(\vec{k} + \vec{G})|\vec{k} + \vec{G}\rangle$. The limit of an isolated nanowire is $F \to \infty$, and the plane wave expansion becomes a continuous transform for transverse $|\vec{k} + \vec{G}\rangle$ vectors. The artificial superlattice of nanorods can be thought of as a device for making a symmetric discretization of this continuous Fourier transform. The translational eigenlabel $\vec{k}$ has a z-component of typical magnitude $k_z \le \pi/c$, and small transverse components $k_\perp \le \pi/Fa$. These transverse components of $\vec{k}$ just fix phase relations on irrelevant parallel nanowires, and should not alter the wavefunctions on the central nanowire. The factor F is sufficiently large, and the corresponding transverse size of the Brillouin zone is so small that transverse components of $\vec{k}$ in the Brillouin zone are essentially 0 anyway.

Now the orthonormal basis set $|\vec{k} + \vec{G}\rangle$ needs to be symmetrized. The reciprocal lattice vectors come in layers $\vec{G} = (\vec{Q},G_z)$, where $\vec{Q}$ is a 2-vector in the $x-y$ plane and G_z is $2\pi\gamma/c$, with γ an integer. The nonzero Q's come in symmetry-equivalent sets, or stars, of ρ vectors $R^\lambda\vec{Q}$. For each separate star s of basis functions $|\vec{k} + \vec{G}\rangle$, we construct

a transformed orthonormal basis $|kmsG_z\rangle$ using

$$|kmsG_z\rangle = \frac{1}{\sqrt{\rho}} \sum_{\lambda} e^{-im\lambda\phi} |R^{\lambda}Q, k + G_z\rangle \qquad (7)$$

From this, we read off the matrix elements of U, namely

$$\langle kmsG_z|U|\vec{k} + \vec{G}\rangle = \frac{1}{\sqrt{\rho}} e^{-im\phi_G} \qquad (8)$$

There are also basis functions with $\vec{Q} = 0$, that is, composed from reciprocal lattice vectors with $n_1 = n_2 = 0$. These already transform according to the $m = 0$ symmetric representation of the rotations, so the relevant entries in the matrix U are just diagonal 1's in the $m = 0$ block.

The possible use of this is that a pre-existing plane wave code can be modified as follows. The Hamiltonian matrix is set up as usual in the $|\vec{k} + \vec{G}\rangle$ basis. The $\vec{k}$ vector is (0,0,k), that is, $k_x = k_y = 0$. The matrix U is computed once and stored for all subsequent iterations. The block-diagonal Hamiltonian submatrices are then found by matrix multiplication. The relevant eigenvectors are then computed for the submatrices. Finally, the inverse transformation recovers the wavefunctions in their unsymmetrized plane wave form because this form is needed for solving Poisson's equation and all the subsequent normal steps of the otherwise unaltered code. Modern plane wave density functional (DFT) codes would not necessarily be improved by this because iterative multiplication $H\psi$ provides a Lanczos-type method of finding low energy states without need to construct the matrix H. These codes exploit the fact that kinetic energy is diagonal in $\vec{k}$ space and potential energy in $\vec{r}$ space. Fast Fourier transforms are needed to make this efficient and require unsymmetrized plane waves to be repeatedly transformed. The additional multiple $U^{+}\psi$ multiplications, even though fast, may add too much computational overhead.

In principle, the same symmetrization procedure works in two other situations, namely (1) a finite nanocrystal or cluster (sometimes called a colloidal quantum dot) with high symmetry, and (2) a symmetrical point defect in a bulk crystal. A cluster code would, of course, usually have local basis functions, and symmetrization is usually built in. However, bulk codes can also be used, with an artificial superlattice. The Brillouin zone is small in all directions, and the translational eigenlabel $\vec{k}$ is needed only for $\vec{k} = 0$. The corresponding unitary transformation follows from the same ideas as for a nanowire. Such a symmetrized bulk code was recently constructed by Chang et al.[7] for supercell defect calculations.

As a toy model for pedagogical purposes, return again to the hcp minimal nanowire shown in Figure 1. As basis functions, a minimal set of local orbitals can be used. The figure shows the schematic appearance of the symmetrized $|s\rangle$ orbital in panel (a), belonging to rotational quantum number $m = 0$ or $m = 3$ depending on the algebraic signs attributed to the two shades of blue. The other two panels show how $m = 0$ symmetrized versions of $|p_x\rangle$ and $|p_y\rangle$ orbitals are constructed. These symmetric orbitals can then be distributed by z-translations with whatever phase factor e^{ikz} is appropriate.

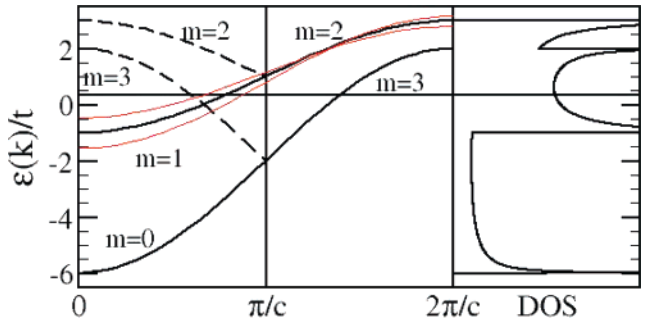

Figure 2. Energy bands of the nanowire shown on the left in Figure 1. A single s orbital per site is assumed, with hopping matrix element $-t$. Energy is vertical in units of t. The horizontal line is the Fermi energy at half-filling (one electron per atom.) The red curves show how the $m = \pm 1$ and ± 2 levels split in a longitudinal field with 0.1 flux quantum per hexagonal cross-section. For k near 0, the lower red line is $m = -1$, while for larger k, the sign reverses.

To be completely simple, consider the case of a single $|s\rangle$ orbital per site. In nearest-neighbor two-site approximation, each orbital overlaps the orbitals on the two atoms in the same plane $z = z_0$, and on two atoms each in the planes directly above and below, $z = z_0 \pm c/2$, where $c/a = \sqrt{8/3}$ gives all six neighbors the same separation, and the same Hamiltonian overlap matrix element $H_{ss\sigma} = -t$. Using the symmetrized states, eq 1, the Hamiltonian is fully diagonalized, with diagonal elements

$$\frac{\epsilon(km)}{t} = -2\cos\left(\frac{2\pi m}{3}\right) - 4\cos\left(\frac{kc}{2}\right)\cos\left(\frac{\pi m}{3}\right) \qquad (9)$$

These energy bands are plotted in Figure 2. The picture is simplified by unfolding to a double Brillouin zone using the "modular" symmetry $\epsilon(k,m + 3) = \epsilon(k + 2\pi/c,m)$, which was discussed in paper II about vibrations.[6] This is a particular case of a general symmetry of states with screw rotation. The phase modulation obtained from $m \rightarrow m + \rho/2$ is the same as that obtained from $k \rightarrow k + 2\pi/c$.

The $m = 0,3$ levels have 0 or 2 longitudinal nodal planes between atoms on a single layer and can be called "*sigma* bands". The $m = \pm 1,\pm 2$ levels correspond to "*pi*-bands". Notice that the *sigma* and *pi* bands overlap. There is no gap in the spectrum, so for one electron per atom or any other partial filling, the model describes a 1-D metal. However, the Fermi-level crossings k_{Fm} are not related by simple ratios, so the metal may be less susceptible than a linear chain to instabilities such as the Peierls distortion.[8]

Just as in clean solids, translational symmetry gives a $\Delta k \approx 0$ selection rule for optical absorption. Just as in molecular physics, the rotational quantum number gives dipole selection rules $\Delta m = 0$ for light polarized along the symmetry (z) axis, and $\Delta m = \pm 1$ for light polarized transverse (x or y directions). In a metallic nanowire, there is a $\Delta m = 0$ transition possible from a state ($k_F - \delta$,m) just below the Fermi level to a state ($k_F + \delta$,m) just above, where the

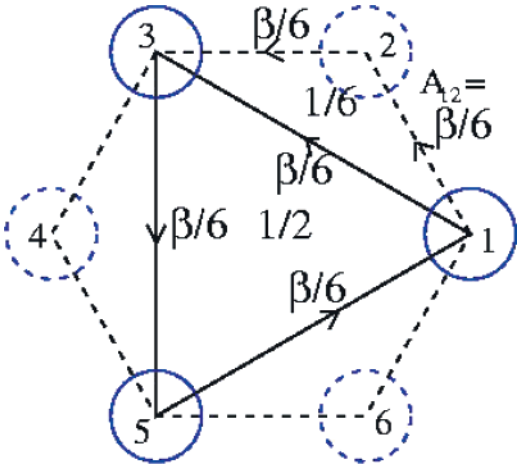

Figure 3. The minimal hcp nanowire in a longitudinal magnetic field B. Peierls phase factors $e^{i\beta/6}$ are attached to tight-binding matrix elements coupling atoms as shown by arrows. The factor Φ in the phase $\beta = 2\pi\Phi/\Phi_0$ is the flux $B \times \sqrt{3}a^2/2$ through a hexagon. When the phases of any closed loop are added, the resulting total phase is $2\pi\Phi_{loop}/\Phi_0$.

wavevector 2δ of the photon is small and can be approximated often by zero. The energy of the transition is $\omega = 2\delta v(km)$, where $v(km)$ is the group velocity, $d\epsilon/d(\hbar k)$. In a nanowire long enough that propagation is interrupted by collisions, that is, not ballistic, the small ω is broadened to $1/\tau$ in the familiar Drude fashion, where $1/\tau$ is the collision rate. These Drude transitions are only allowed for z-polarized light. To light polarized transversely, a metallic nanowire looks like a semiconductor, with a finite gap to optical excitation, from a state (k,m) somewhere below the Fermi energy to a state $(k,m \pm 1)$ of different energy somewhere above the Fermi energy. For the minimal nanowire shown in Figure 1, the minimum energy transverse excitation energy is $\hbar\omega \approx 1.88|t|$, and the maximum transverse single electron−hole pair excitation energy is $\hbar\omega \approx 2.85|t|$. It seems likely that nonmetallic transverse response will remain even when there is no rotational symmetry and therefore no transverse rotational selection rule $\Delta m = \pm 1$. Interband scattering can certainly allow Drude response to spread to transverse response channels, but in a clean nanowire, this would probably not happen. In any event, use of rotational symmetry gives a simplified understanding of nanowire optical response.

The states $m = 0,3$ do not carry circulating currents, but $m = \pm 1$ and $m = \pm 2$ do. To see this, consider the effect of an applied magnetic field along the z-axis. The B-field is described by a modification of the tight-binding matrix elements known as the "Peierls substitution" (Figure 3).[9,10] Each matrix element t_{ij} is multiplied by the phase e^{iAij} where

$$A_{ij} = (2\pi e/h) \int_{\vec{R}_j}^{\vec{R}_i} d\vec{s} \cdot \vec{A} \qquad (10)$$

and where $\vec{A}$ is the vector potential. There is a particularly symmetric gauge where the phases A_{ij} are all equal to $\beta/6$, where β is 2π times the flux Φ through a hexagonal cross-section, divided by $\Phi_0 = h/e$, the flux quantum. Because of this high symmetry, the Hamiltonian continues to be diagonal, with energy eigenvalues modified to

$$\frac{\epsilon(km,B)}{2t} = -\cos\left(\frac{2\pi m}{3} + \frac{\beta}{6}\right) - 2\cos\left(\frac{kc}{2}\right)\cos\left(\frac{\pi m}{3} + \frac{\beta}{6}\right) \qquad (11)$$

When multiples of 6 flux quanta thread the hexagon, each loop has an integer number of flux quanta, and the energy levels return to their zero field values. If we use the nearest-neighbor lattice spacing of elemental Zn, $a = 2.665$ Å, the periodicity in B occurs at 4×10^5 T, 4 orders of magnitude larger than lab fields. For weak fields, the $m = \pm 1$ and $m = \pm 2$ levels split linearly. The $k = 0$, $m = \pm 1$ levels split by $\pm\mu B$, where $\mu/\mu_B = 3ma^2t/2\hbar^2$, a number of order 1, μ_B being the Bohr magneton. The result for a field 0.1 Φ_0 per hexagon is shown in Figure 2. The splitting in the $m = \pm 2$ level changes sign at $k = 2\pi/3c$.

Apart from the interesting k- and m-dependent anisotropic orbital magnetism, the existence of a rotational quantum number m has other technical implications. Cooper pairing, for example, will involve (k,m) pairing with $(-k,-m)$. Chang et al.[1] have already solved exciton problems in nanowires using the (k,m) quantum numbers. Scattering selection rules will have not just k conserved *modulo* $2\pi/c$, but also m conserved *modulo* ρ. Real nanowires will be perturbed away from the ideal symmetry assumed here. Nevertheless, model calculations built on use of this symmetry should be very useful for technical simplifications of theory, even for nonideal nanocrystalline nanowires, in cases where the global symmetry is not the prime determinant of behavior.

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