Electronic structure of periodic minimal surfaces — ‘topological band structure’

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Electronic band structure for electrons bound on periodic minimal surfaces is differential-geometrically formulated and numerically calculated. We focus on minimal surfaces because they are not only mathematically elegant (with the surface characterized completely in terms of ‘navels’) but represent the topology of real systems such as zeolites and negative-curvature fullerenes. The band structure turns out to be primarily determined by the topology of the surface, i.e., how the wavefunction interferes on a multiply-connected surface, so that the bands are little affected by the way in which we confine the electrons on the surface (thin-slab limit or zero thickness from the outset). Another curiosity is that different minimal surfaces connected by the Bonnet transformation (such as Schwarz’s P- and D-surfaces) possess one-to-one correspondence in their band energies at Brillouin zone boundaries.

I. INTRODUCTION

There is a long history for the fascination in particles bound on curved surfaces, which dates back to the early days of quantum mechanics. There are two complimentary points of interests: one is how the particle motions are affected by the local curvature of the surface. The other is how the global topology (i.e., how the surface is wound) affects quantum mechanical wave functions. The latter problem becomes especially interesting if we consider a periodic surface embedded in the three-dimensional space.

Geometrically, Schwarz, back in the 19th century, showed that we can make curved surfaces extend over the entire three-dimensional space by connecting hyperbolic (i.e., everywhere negatively curved) patches. Specifically, Schwarz has constructed periodic minimal surfaces, where minimal means that the negatively-curved surface has a minimized area with the mean curvature \( \frac{1}{2}(\kappa_1 + \kappa_2) \) with \( \kappa_1, \kappa_2 \) being the principal curvatures) vanishing everywhere on the surface.

There are reasons from both mathematics and condensed-matter physics why periodic surfaces are intriguing. First of all, periodic surfaces are of general interest in the condensed-matter physics. (i) In general, ‘crystals’ (periodic structures) composed of surfaces are conceptually interesting as a class of periodic system on which electrons move. Mackay has classified them group-theoretically (just as the ordinary crystals composed of atoms are classified with the space group), which he named ‘flexi-crystallography’.

(ii) In terms of model sciences, periodic minimal surfaces represent the topology of real condensed-matter systems. These include not only conventional materials such as zeolites or a silica polymorph called melanophlogite, or isostructural silicon clathrates, but recent advances in fabrication of exotic materials such as fullerenes or nanotubes have inspired further possibilities such as negative-curvature fullerene (or C\(_{60}\) zeolite) whose fabrication has been attempted with a zeolite as a template. Their structures can be modeled as curved surfaces if we smear out atoms into a surface in the effective-mass sense, and it is a fundamental question to consider how a mobile (e.g., \( \pi \)) electron behaves on such surfaces.

Second, there are mathematical interests and simplifications when a periodic surface is minimal: we can exploit the Weierstrass representation, which enables us to specify the surface in a surprisingly simple manner in terms of ‘navels’. The representation also simplifies Schrödinger’s equation as we shall show in the present paper.

There are further mathematical fascinations specific to surfaces. One virtue of the structure constructed from surfaces is we can deform it. One can in fact deform one minimal surface into another with a differential geometrical transformation called the Bonnet transformation. We can then raise a question of how the band structure for one surface could be related with that for the transformed one. Another interest is that some periodic minimal surfaces, such as Schwarz’s P-surface, have a high symmetry (‘interior-exterior’ symmetry) that divides the space into two equivalent parts, which should be reflected in the electronic band structure.

So in the present paper we address ourselves a question: how the electronic band structures should look like for periodic minimal surfaces. To start with, however, we have to envisage there are in general two ways (Fig.) to make electrons confined to a surface: (a) One is to consider electrons bound to a thin, curved slab of thickness \( d \), where the limit \( d \to 0 \) is taken. (b) The other is to consider the surface with the degree of freedom normal to the surface ignored from the outset, i.e., a two-dimensional sheet is rolled into the curved surface. Either way it
has been shown that an effective potential arises from the curvature of the surface, but that the potential is different between the two cases. Namely, the thin slab case (a) has a potential

\[-(\hbar^2/8m)(\kappa_1 - \kappa_2)^2,\]

while the case (b) has

\[+(\hbar^2/8m)(\kappa_1 + \kappa_2)^2.\]

The origin of the discrepancy was subsequently revealed by Nagaoka and coworkers when the degree of freedom normal to the surface is ignored. Dirac’s prescription for constrained systems can be applied, but there is a room for ambiguity in the order of operators. If we adopt the conservation constraint, the resultant equation reduces to that in the \(d \to 0\) approach. When the surface is minimal (\(\kappa_1 + \kappa_2 = 0\)), the curvature potential is nonzero in general (since \(\kappa_1 - \kappa_2 = 2\kappa_1 \neq 0\) in case (a), while the curvature potential vanishes identically in (b).

For condensed-matter systems such as atoms arrayed along a curved surface, we should take the \(d \to 0\) approach. Still, the difference in the band structure between the two cases is curious. Namely, although we have a periodic system in either case, the periodicity imposed in case (a) is the periodicity in the strong potential that confines the electron into a thin slab (Fig.1(a)), while in the case (b) the electron moves freely along the surface, where the only constraint is that an electron has to move in a space having a nontrivial topology. The topology can have a profound effect on the electron’s wave function, since, if we regard the periodic surface as a network in a space having a nontrivial topology. Thus the periodicity felt by an electron amounts to the strong confinement potential in case (a), while the periodicity only enters the ‘d’ band into \(E\) of the band structure (band splitting, such as a split of the ‘g’ band into \(E_g\) and \(T_{2g}\), and band widths) is also universally \(\Delta^2/2mL^2\) with \(L\) being the linear dimension of the unit cell of the periodic surface. (iii) We go further to ‘Martensitic-deform’ a surface to another connected by the Bonnet transformation. We shall show that there exists a curious one-to-one correspondence in their band structures, which illustrates another curious feature in the topological band structure.

II. WEIERSTRASS REPRESENTATION OF MINIMAL SURFACES

We start with a mathematical prerequisite for representing minimal surfaces. A two-dimensional surface \(r(q^1, q^2)\) embedded in a three-dimensional space can be expressed in terms of two dimensional coordinates \(q^1, q^2\), where \((q^1, q^2) \equiv (u, v)\) are called isothermal when the metric tensor \(g_{ij}\) is diagonal with

\[dr \cdot dr = g_{11}(du^2 + dv^2)\]

What Weierstrass and Enneper have found is that a necessary and sufficient condition for \(r(u, v)\) representing a minimal surface with isothermal \((u, v) \in S\) (S: a simply connected region) is that there exist \(F, G\), functions of \(w \equiv u + iv\), with which \(r(u, v) = (x(u, v), y(u, v), z(u, v))\) is expressed as

\[
\begin{align*}
\mathbf{r}(u, v) &= \text{Re} \left( \int_{w_0}^w F(1 - G^2) \, dw, \\
&\int_{w_0}^w iF(1 + G^2) \, dw, \int_{w_0}^w 2FG \, dw \right),
\end{align*}
\]

where \(w_0\) is a constant, and \(FG^2\) is assumed to be regular (i.e., \(m\)-th poles of \(G\) assumed to coincide with \(2m\)-th zeros of \(F\)) if there are singularities that violate this condition, we can exclude these points by incising cut(s) to make \(S\) a Riemann surface. Thus there is a one-to-one correspondence between a minimal surface and the functional form of \(F, G\).

Now, Schrödinger’s equation for a curved surface, expressed with two dimensional coordinates \((q^1, q^2)\) and metric tensor \(g_{ij}\), is written as

\[
\left[-\frac{\hbar^2}{2mG} \frac{\partial}{\partial q^i} \sqrt{g} g^{ij} \frac{\partial}{\partial q^j} - \frac{\hbar^2}{8m} (\kappa_1 - \kappa_2)^2\right] \psi(q^1, q^2) = E \psi(q^1, q^2),
\]

where summations over repeated indices are assumed. This equation is for model (a), while we can replace the second term in the bracket (potential term) by \(\pm \hbar^2/(2m) (\kappa_1 + \kappa_2)^2\) for model (b).

In the Weierstrass-Enneper representation, every quantity in the Schrödinger’s equation can be expressed in terms of \(F\) and \(G\), since the Laplacian in the isothermal coordinates in eq.1 reduces to \((\partial^2/\partial q^2)/\sqrt{g}\) in the isothermal coordinates, where

\[g \equiv \det \{g_{ij}\} = \left[ \frac{1}{2} |F|(|G|^2 + 1) \right]^4,
\]

while we can plug in \(\kappa_1 = -\kappa_2 = 4|G'/|G||(|G|^2 + 1)^2\) for the curvature term. Schrödinger’s equation for periodic minimal surfaces then reduces to
including P-surface). In this case we can exploit the stereo-
periodic (periodic in $G(w)$). After a bit of algebra, we finally arrive at the differential equn. 5 below).

\[ \frac{4}{|F|^2((|G|^2 + 1)^2 \left( \frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2} + \frac{4|G'|^2}{(|G|^2 + 1)^2} \right) \psi = \varepsilon \psi, \]

where $\varepsilon \equiv E/(\hbar^2/2m)$. As evident from the Weierstrass representation (figure), $F$ has the dimension of length and $G$ is dimensionless. Hence the energies in minimal surfaces always scale as $E/(\hbar^2/2mL^2)$, where $L \sim F \sim \text{linear}$ dimension of the unit cell (a precise expression given in eqn. 6 below).

We can have a more transparent form when $G(w) = w$ (as is often the case with periodic minimal surfaces, including P-surface). In this case we can exploit the stereographic map (Gauss map) from the infinite complex plane $(u, v)$ to a unit sphere $(\theta, \phi)$,

\[ w = u + iv = \cot \left( \frac{\theta}{2} \right) e^{i\phi}. \]

After a bit of algebra, we finally arrive at the differential equation for $(\theta, \phi)$,

\[ \left( 1 - \cos \theta \right)^4 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta \partial \phi^2} + 1 \right) \psi = \varepsilon \psi. \]

Curiously, a common coefficient $(1 - \cos \theta)^4/|F|^2$ factors out for the Laplacian (the first three terms in the large parentheses in the above equation) and the curvature potential $(+1)$, which is made manifest due to the Weierstrass potential ($\pm 1$), as shown in Fig. 2. With the stereographic mapping discussed above, a unit cell is mapped onto two spheres, connected into a Riemann surface via four cuts, which have to be introduced to make $FG^2$ non-singular since $F$ has poles.

Differential geometrically $F$ is in general specified solely by such poles in a form $F \propto 1/\prod (w-w_i)^\eta$ where $\eta$ determines the topology of the surface. In fact the poles correspond, in the language of differential geometry, to the navel points (umbilical points), which are defined as the points where every cross section is inflected, with the two principal curvatures becoming degenerate, $\kappa_1 = \kappa_2 (= 0$ for a minimal surface). So a periodic minimal surface is completely characterized by the navels that appear periodically. The curvature potential $\propto -(\kappa_1 - \kappa_2)^2$ in case (a) varies on the surface, which may be called a ‘crystal field’ in flexi-crystals. Navel then specify the positions where the curvature potential becomes maxima ($= 0$), while the minima occurs at the maxima of the absolute value of $\kappa_1 (= -\kappa_2$ for a minimal surface). In the P-surface the navels (potential maxima) occur at eight ‘Affenstall’ (monkey’s-saddle) points in a unit cell, while the potential minima occur at four points around each nape of the neck as depicted in Fig. 2(a).

IV. RESULTS FOR THE BAND STRUCTURE

Band structure for case (a) In Schrödinger’s equation for periodic minimal surfaces, eqn. (6), the variables $\theta, \phi$ cannot be separated, so that we have solved the equation numerically by discretizing $\theta, \phi$ to diagonalize the Hamiltonian matrix. In discretizing the spherical coordinates, a special care is taken around the navels, since the Jacobian $J$ of the transformation to the Gauss sphere is singular there (Fig. 3). The band structure is obtained by connecting the adjacent unit cells with appropriate phase factors.

We now come to the result for the band structure for the P-surface in Fig. 4 (curves), and typical wavefunctions at $\Gamma$ and $H$ in the bcc Brillouin zone ($\Gamma$ in the simple-cubic zone) in Fig. 5. The P-surface happens to divide the space into two equivalent parts, since a body center enclosed by the surrounding unit cells has the same shape as the original unit, so that we first note that the true symmetry is body-centered cubic rather than simple cubic. So the bands are displayed on the Brillouin zone for bcc. In accord with the above argument, the energy scale (band width, splitting etc) is $\sim \hbar^2/2mL^2$. This is of the order of 1 eV for $L \sim 10 \AA$, the unit cell size assumed for a hypothetical negative-curvature fullerene.

The curvature, or the effective mass, of these bands are either positive (electron-like) or negative (hole-like) according to the nature of the wave function. The mass cannot be estimated with a simple $k \cdot p$ perturbation, since the perturbation $\propto k \cdot p$ derives from the fact that $H_0 \propto p^2$ while $H_0$ has no such simple form on a curved surface. In other words, the $k \cdot p$ formula has $\sum_p (\langle j|p|j \rangle \langle j|p|j \rangle)/(E_i - E_f)$, so we would have to calculate the matrix elements of $p$ for wavefunctions that
are finite only along the surface.

**Band structure for case (b)** Now we are in position to compare the (a) confinement case (curves in Fig. 1) with the (b) rolled case (dotted lines in Fig. 1). We can immediately see that the two band structures are rather similar up to some offset ($2.34h^2/2mL^2$). This is surprising, since there is no apriori reason why they should be. To be more precise quantitative features characterizing the band, i.e., the effective mass and band widths, are similar between the two cases. So we conclude that the band structure does not essentially depend on the way in which electrons are confined, at least for ‘gently’ curved surfaces such as minimal surfaces where the there are no sharp edges that would give large curvature potentials.

V. BONNET TRANSFORMATION

The next important question is: are the band structures for surfaces connected by the Bonnet transformation related?

**Bonnet transformation** The deformation of the P-surface to other periodic minimal surfaces can be implemented by the Bonnet transformation, which is conformal and is represented by an elliptic transformation. A beautiful asset of the Weierstrass representation for minimal surfaces is that the Bonnet transformation is simply represented by a phase factor, $F \rightarrow Fe^{i\beta}$, in eqn. (1), where $\beta$ is called the Bonnet angle. If we apply this to the P-surface (cubic), the transformation changes it into the G-surface (gyroid with $\beta = 0.211\pi$) and the D-surface (diamond with $\beta = \pi/2$), which may be regarded as a ‘Martensitic transformation’ in the words of Ref. 27. The structure of the D-surface is depicted, along with the P-surface, in Fig. 2. Since the D-surface has a diamond symmetry, its unit cell contains two ‘cages’.

We can first note that the Bonnet transformation preserves the metric tensor and the Gaussian curvature. This implies that all the surfaces connected by the Bonnet transformation obey the identical Schrödinger equation within a unit patch. Indeed, if we look at Schrödinger’s eqn. (1), $F$ only enters as $|F|$, so that $F \rightarrow Fe^{i\beta}$ does not alter the equation. Although this is curious enough, this does not mean that the band structures are identical, since, while the transformed surfaces share the same genus (= three for P and D), the way in which unit cells are connected is different among them.

**Band structure of a Bonnet-transformed surface**

Figure 2 compares the band structures for the P- and D-surfaces. The two band structures are indeed different due to the difference in three dimensional connection of the unit cells discussed above. Curiously, however, we find that the values of the band energy at special points (Brillouin zone corners, edges and face-centers) have identical set of values between different surfaces. Namely, a close comparison of the two band structures reveals that the band energies exactly coincide, where the ‘law of correspondence’ is

| P-surface   | D-surface |
|-------------|-----------|
| $F$, $H$    | $\Gamma$, $R$ |
| $N$         | $X$, $M$  |

This can be explained from the property of the Bonnet transformation that does not change Schrödinger’s equation. For this purpose we have to look at the unit cells more closely. In Fig. 3(a), we show how unit patches are connected for the D- and P-surfaces. We have indicated in the figure how the eight patches in a unit cell, numbered with 1 through 8, are connected to other patches in the adjacent cells by marking the edges with those numbers (i.e., if an edge is marked with, say, 7, the adjacent patch should be 7). The wave function should be continued to the adjacent patch with a certain phase factor. We have indicated the connection coefficients,

$$\rho_i = \exp(i\phi_i),$$

where $\phi_i$ is the Bloch phase along $i = x, y, z$. Hence this diagram fully characterizes how the Bloch wave functions are connected on the periodic minimal surfaces in terms of patches. We can then compare the coefficients for the P- and D-surfaces to extract a correspondence at special points in $k$-space.

The diagrams introduced here have naturally different patch numbers assigned on them between the P- and D-surfaces, since the way in which the patches are connected (i.e., numbers attached to the edges) is different between them. However, we can make them identical, if we rearrange the connection numbers by noting the symmetry. Since the parity inversion $\sigma_p$ with respect to the center of a unit cell preserves the Hamiltonian and does not change the special $k$-vectors on the zone edges either, the group theory dictates that the eigenstates on those $k$-points should have the parity 1 or -1. Then we can always construct the wave function for one half of the unit cell by multiplying the wave function for the other with 1 or -1. Namely, if we employ a simple cubic unit cell for the P-surface (Fig. 4, which is twice the bcc unit cell depicted in Fig. 3(a)) to make the correspondence clearer, an application of $\sigma_p$ to the upper half?, the lower turns out to have just the same connection number $s$? as in the D-surface as shown? in Fig. 3(b). So we have now the same connection numbers between P and D, where the only difference is different connection coefficients ($\rho_i$’s) between P and D as indicated in the figure. If we compare these, we end up with a ‘law of corresponding $k$-points’,
between the simple-cubic and bcc unit cells.

The wave functions shown in Figs. 7 are actually related through this relation. A simplest way to confirm this is to note that the wave function on each unit patch behaves in a similar manner. In fact, the wave function \( \psi(\theta, \phi) \) in eqn. 6 is identical between the two surfaces.

VI. DISCUSSIONS

The band structures revealed here should have important implications on various physical properties. These should include transport properties as well as the cyclotron resonance, which can detect the effective mass arising from topological band structures. Since the mass is determined by the interference of wave functions, effects of external magnetic fields should also be interesting.

We can finally comment that, if we adopt foams of graphite to realize curved surfaces, then the equation of motion of \( \pi \) electrons on the network of the honeycomb lattice will become, in the effective mass picture, the problem of zero-mass Dirac equation (i.e., Weyl’s equation) on curved surfaces. While we have ignored spin degrees of freedom here, the spin connection on the surface will give rise to a Berry’s geometrical phase.

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FIG. 1. Two ways to prepare a surface: (a) to introduce potential barriers that confine electrons in a three-dimensional space to a thin membrane, or (b) to roll a sheet of free electrons into the curved surface.

FIG. 2. The structures of P(a) and D(b) surfaces. We show a unit patch on the left panel, and a full unit cell on the right. The grey-scale in the right panel represents the curvature potential, where shaded (open) circles depict potential minima (maxima, coinciding with the navels). (c) The stereographic projection from minimal surface to Gauss spheres. A unit patch of P or D corresponds to a pair of 1/8 spheres.

FIG. 3. Descretization for the spherical coordinates: (a) a mesh with even intervals in \( \theta \) and \( \phi \) and (b) uneven ones, adopted here, which take care of the singular point in the Jacobian.

FIG. 4. The energy band structure in units of \( \hbar^2/2mL^2 \) is shown for the P-surface, when the curvature potential is considered (curves) or ignored (dots) with an energy offset to make the band bottoms coincide between the two cases. The inset depicts the Brillouin zone for a bcc unit cell.

FIG. 5. Typical wavefunctions for a unit cell of P-surfaces with positive (negative) amplitudes color-coded in red (blue). Their eigenenergies are indicated in Fig. 4.

FIG. 6. The band structures for the P- and D-surfaces. Horizontal lines indicate how the energies at the zone center or edges coincide between the two cases.

FIG. 7. Typical wavefunctions for a unit cell of the Bonnet-connected P- and D-surfaces with positive (negative) amplitudes color-coded in red (blue). Their eigenenergies are indicated in Fig. 4.

FIG. 8. (a) The way in which patches (labeled by large numbers) are connected to those in adjacent unit cells are indicated by small numbers attached to the edges for the D-surface. The Bloch phase factors (\( \rho_i \)'s) are also shown. In the left panels the patches are flattened and expanded, while the right panels depict the actual three-dimensional shapes. (b) The corresponding diagram for the P-surface, where we have rearranged the numbers to make them identical with those for the D-surface by exploiting the symmetry. Accordingly the Bloch phase factors for the P-surface involve the parity inversion (\( \sigma_p \)). An example is shown in (c), which indicates how patches 7,8 are neighboring 3,4 through \( \rho_i \sigma_p \).

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