

Chubb, S.R. *Nuts and Bolts of the Ion Band State Theory*. in *Tenth International Conference on Cold Fusion*. 2003. Cambridge, MA: LENR-CANR.org. This paper was presented at the 10th International Conference on Cold Fusion. It may be different from the version published by World Scientific, Inc (2003) in the official Proceedings of the conference.

Nuts and Bolts of the Ion Band State Theory

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The Nuts and Bolts of our Ion Band State theory of low energy nuclear reactions (LENR's) in palladium-deuteride (PdD) and palladium-hydride (PdH) are the electrons that hold together or tear apart the bonds (or lack of bonds) between deuterons (d's) or protons (p's) and the host material. In PdD_x and PdH_x, this bonding is strongly correlated with loading. In ambient loading conditions ($x \ll 0.6$), bonding inhibits Ion Band State occupation. As $x \rightarrow 1$, slight increases and decreases in loading can induce "vibrations" (which have conventionally been thought to occur from phonons) that can induce potential losses or increases of p/d. Naive assumptions about phonons fail to include these losses and increases. These effects can occur because neither H or D has core electrons and because in either PdD or PdH, the electrons near the Fermi Energy have negligible overlap with the nucleus of either D or H. In the past, implicitly, we have used these facts to justify our Ion Band State theory. Here, we present a more formal justification, based on the relationship between H(D) Ion Band States (IBS's) and H(D) phonons that includes a microscopic picture that explains why occupation of IBS's can occur in PdD and PdH and how this can lead to nuclear reactions.

1 Introduction

Previously, we suggested that as $x \rightarrow 1$, to minimize energy, a small number of the deuterons (d's), found in deuterium (D) atoms in a PdD_x host, or of protons (p's), in hydrogen (H) atoms in PdH_x, could occupy wave-like, Ion Band States (similar to the kinds of itinerant, wave-like states that electrons occupy in solids). We also suggested that subsequently, once in Ion Band States (IBS's), d's could have such significant overlap with each other that a distinctly different form of nuclear reaction might occur at many periodically equivalent locations, simultaneously. Thus, we predicted that d's and p's could react in a solid but that the processes would be dominated by $d+d \rightarrow {}^4\text{He}$ reactions and would occur without appreciable energy or momentum transfer within bulk regions (where periodic order was assumed to be present), to regions outside the bulk, and without appreciable radiation or high energy particles.

One limitation of this picture is its qualitative description of the coupling between electromagnetic- and nuclear- scale effects and larger length-scale coupling to the lattice. A second reason the theory has not been widely accepted, despite the fact its predictions have been independently borne out by experiment¹, is the seemingly counter-intuitive limit where it applies: when d/p can become wave-like and react in a nuclear fashion, to minimize total electromagnetic energy, through processes that are manifestly static, and non-dynamic.

In the paper, we summarize key features of our model, which include the possibility of ion transport into and away from a PdH or PdD host, as well as additional quantum mechanical effects involving ion transport, based on a natural generalization of electron band theory, in which "phonons" involving p, d, and, implicitly, tritons (t) are replaced by IBS's involving p, d, or t. The generalization of the earlier model justifies: 1. Our energy minimization procedure, 2. The conclusion that heat and by-products are required to be released with low energy, near surfaces, and 3. A more refined estimate of the minimal crystal size that is required to initiate the reaction process.

2 Phonons and Ion Band States in PdH and PdD

2.1 Phonons in Infinitely Ordered Solids

In the conventional phonon problem, vibrations are introduced by allowing for a small displacement $u(\equiv u(\mathbf{R}_{n,\alpha}))$ of an individual atom (at position τ_α), relative to its equilibrium location $r'=\mathbf{R}_{n,\alpha}$ ($=\tau_\alpha-\mathbf{R}_n$), in a unit cell, centered at a Bravais vector² \mathbf{R}_n . Each vibration is assumed to occur in response to a well-defined (attractive) restoring force that acts on the atom to drive it towards the location ($\mathbf{R}_{n,\alpha}$) that the atom would have in a static lattice (defined by temperature $T=0$, in an ordered solid), where the net force, acting on any atom vanishes ($-\nabla_{\mathbf{r}} \mathbf{V}|_{U(\mathbf{r}')=0} = \mathbf{0}$, V =total potential energy). This restoring force is introduced through the difference in relative positions, $R-R_e + u(R)-u(R_e)$ between atoms at locations $r= R+u(R)$ and $r'=\mathbf{R}_e - u(\mathbf{R}_e)$ and involves differences of the form $(u(\mathbf{R}_{n,\beta})-u(\mathbf{R}_{n',\beta}))^{x_j}$ ($x_j=x$, $x_j=y$, or $x_j=z$, respectively, for $j=1, j=2$, or $j=3$), which also can be expressed in a more general way: $u(\mathbf{R}_{n,\alpha})-u(\mathbf{R}_{n',\alpha})^{x_j} = (u(\mathbf{R}_n)-u(\mathbf{R}_{n'}))^{j'}$ (where $\mathbf{j} = \mathbf{j}(\beta) = j'+(j_\beta-1)3$; $j'=1,3$, $\mathbf{R}_{n,\beta}(j_\beta)=\mathbf{R}_n - \tau(j_\beta)$, $\tau(j_\beta)$ = location of a particular atom associated with the value of $j_\beta=1, N_{\text{atom}}$, and N_{atom} =number of atoms per unit cell). Then, when V only depends on the relative separations ($r-r'$) between atoms,

$$V = V_{\text{eq}} + \sum_{\mathbf{k}, i, j} U^i(\mathbf{k})^* D_{i,j}(\mathbf{k}) U^j(\mathbf{k}), \quad (1)$$

where $U^i(\mathbf{k})$ is a "normal mode", defined by the discrete fourier transform of $u(\mathbf{r})$,

$$U^i(\mathbf{k}) = \sum_{\mathbf{R}_n} \frac{\mathbf{u}^i(\mathbf{R}_n) \mathbf{e}^{i\mathbf{k} \cdot \mathbf{R}_n}}{\sqrt{N}}. \quad (2)$$

$D_{i,j}(\mathbf{k})$ (the Dynamical Matrix) is related to the fourier transform of the gradient of the (attractive) force between pairs of atoms.

Also, it is usually assumed that this discrete fourier transform can be imposed using periodic (Born-VonKarman) boundary conditions $u(\mathbf{R}_n + \mathbf{L}_\alpha) = u(\mathbf{R}_n)$ ($\alpha=1,3$) in each of three independent directions, associated with macroscopically finite displacements (\mathbf{L}_α) that are assumed to be so microscopically large that they do not affect the associated dynamics. From this starting point, heuristically, a mathematically well-defined framework has been used, to investigate vibrations, using wave-vectors \mathbf{k} (associated with Eq. 2) that are confined to the first Brillouin zone, which, as in conventional band theory is defined by the requirement that² $\mathbf{k} = \sum_{\alpha=1,3} \frac{\mathbf{g}_\alpha N_\alpha}{2N_\alpha}$. Here,

\mathbf{g}_α = primitive reciprocal lattice vector[2] (which means that $\mathbf{g}_\alpha \cdot \mathbf{L}_\beta = 2\pi N_\alpha \delta_\alpha^\beta$; δ_α^β = Kronecker Delta Symbol=1 if $\alpha = \beta$; $\delta_\alpha^\beta = 0$, if $\alpha \neq \beta$), $-N_\alpha \leq \mathbf{n}_\alpha \leq N_\alpha - 1$, and there are $2N_\alpha$ unit cells, along a straight line parallel to \mathbf{L}_α (so that the total number of unit cells= $N=8N_1N_2N_3$).

Initially the theory was used to study heat dissipation in insulators and semi-conductors. Subsequently, through Density Functional Theory, it has become possible to apply the theory to metals, provided a specific normal mode $U^i(\mathbf{k})$ becomes dominant. In this limit, when the motion, frequency and deformation of the atom can be treated as being static (frozen), relative to effects associated with electrons, a series of "frozen phonon" calculations, of electronic structure, in which distortions of the lattice are treated as being dynamically uncoupled from the changes in electrons, can be used to infer phonon motion (and related effects). In each of these calculations,

different values of $\mathbf{u}^{i\alpha}(\mathbf{R}_{n,\alpha})$ are derived using a single term, $\frac{U^{i\alpha}(\mathbf{k})}{\sqrt{N}} = dU$ of the inverse fourier transform Eq. 2

(based on the assumption that a single mode is dominant): $\mathbf{u}^{i\alpha}(\mathbf{R}_n) = 2dU \cos(\mathbf{k} \cdot \mathbf{R}_n)$.

2.2 Phonons in PdD and PdH, and their Relationship to Ion Band States

Klein and Cohen (KC) performed frozen phonon calculations in PdD and PdH of "zone center" ($\mathbf{k}=0$) H(D) phonons³, in which H(D) motion at full-loading was modeled using measurements⁴ of optical phonon spectra that were made with ambient loading conditions ($x \sim .6$, in PdD_x and PdH_x), at liquid nitrogen (and higher) temperatures, as opposed to the (valid) full-loading value ($x=1$), where their calculations apply. These authors realized because of large an-harmonic effects, an approximate Schroedinger Equation should be used to quantify the motion of H(D) nuclear centers, as opposed to an alternative model, based on the harmonic approximation. They failed to

distinguish between effects associated with ambient- and full- loading. They also omitted effects related to finite size, external forces and increases in H and/or D. Their simulations (in an infinite, periodic solid, at vanishing temperature $T \sim 0$) may be relevant for determining average quantities in large crystalline hosts.

KC's omissions as well as omissions in other models that treat phonons as being neutrally-charged fail to include a distinctive bonding feature of H and its isotopes in a metallic host: the possibility that the "atomic centers" of H(D) or ^3H (Tritium) can become so mobile that they can "move" in response to externally applied electromagnetic fields. ***This is possible because these atoms do not have core electrons.*** Thus, these atoms can "bond" (or not "bond") to a host in unusual ways in response to small, external forces. These bonding features can induce vibrations (previously identified as phonons), in which the nuclei of these atoms effectively can move in such a way that a "net" accumulation of positive (ion) charge can occur outside the host. Since, effectively, a net accumulation of charge can occur, a more accurate description of these vibrations is that they are an example of the itinerant (wave-like) forms of charge transport (analogous to similar, wave-like forms of charge transport, involving electrons) that we have previously referred to as Ion Band States (IBS's). For the same reason, important assumptions in conventional phonon theory, involving the identification of external forces, must be modified in situations involving H, D, or ^3H adsorption into fully-loaded PdH, PdD, or Pd ^3H . Under ambient conditions these distinctions are inconsequential because a quasi-equilibrium can be established in which external forces approximately vanish. At full-loading, particular features^{3,5} associated with the electronic states in the immediate vicinity of the Fermi Energy (E_f) require that external electrical forces, either directly, or indirectly, be present. But these forces are omitted in simulations based on an infinite solid.

In principle, KC appear to have studied conventional lattice vibrations. In fact, in a finite PdH (PdD) host, they simulated a form of IBS, in an asymptotic $k=0$, semi-classical limit where ion currents vanish. Specifically, when $k=0$, no ion conduction (or transport of a p or d nucleus) occurs. But at finite k , finite conduction can take place. This interpretation of their results applies when a small (macroscopically infinitesimal, but potentially microscopically large) number of H (D) atoms are forced into fully-loaded PdH (PdD). Then, the lowest energy state (which effectively mimics the lowest phonon state in their model) can, in fact, be viewed as the ground state (GS) energy of an IBS, associated with a compound of the form PdD $_{1+\delta}$, where δ (which is $\sim 10^{-3}$ - 10^{-4}) refers to the number of D nuclei per unit cell that occupy IBS's.

In this limit, the lowest lying, vibrational excitations of a finite PdD or PdH host are IBS's as opposed to phonons because they are expected to induce forms of coupling that directly and indirectly affect electrical (and ionic) conduction and are omitted from conventional phonon theory. These long-range forms of coupling are expected to occur because since electronic states near E_f in a PdH or PdD host have negligible overlap with D or H, the addition or depletion of electrons that results when H or D is removed or added to the host can induce changes in electronic structure that are uniformly distributed over many unit cells without appreciably altering the occupation of (other) states that have appreciable overlap with regions where H or D nuclei are located.

Detailed calculations are required to understand the microscopic physics. But to illustrate the relationship between H(D) phonons (as in KC³) to IBS's, it is sufficient to apply the semi-classical model, used in conventional electron conductivity in bulk solids. (Here, a "bulk solid" includes bulk and surface regions.) In the semi-classical limit, in "bulk solids", changes in total charge can be approximately described through changes in the zero of energy (defined by the chemical potential). (In what follows, we do and will distinguish surface from bulk regions, which are both different from "bulk solids".) The total charge within each unit cell vanishes in bulk regions; while in surface regions, a net accumulation of charge in a particular unit cell can take place.

In the limit considered by KC, the relevant zone center phonon Schroedinger equation is

$$\hbar \frac{\partial \Psi(\mathbf{U}(0))}{\partial t} = \left(\sum_{\alpha=1,2} \frac{-\hbar^2 \nabla^2}{2M_\alpha} + V(\mathbf{U}(0)) \right) \Psi(\mathbf{U}(0)) = (\mathbf{T}(\mathbf{u}(\mathbf{R})) + V(\mathbf{u}(\mathbf{R}))) \Psi \quad (4)$$

where $\alpha=1$ or 2, respectively, for the Pd or H (D) atom in PdH (PdD), and T and V are (real space) representations of the kinetic and potential energy, defined (through $\mathbf{U}(0)$) by

$$\mathbf{T}(\mathbf{R}) = -\frac{1}{N} \sum_{\alpha=1,2} \sum_{\mathbf{n}, \mathbf{n}'} \frac{\hbar^2}{2M_\alpha} \nabla_{\mathbf{u}^{i\alpha}(\mathbf{R}_\mathbf{n})} \cdot \nabla_{\mathbf{u}^{i\alpha}(\mathbf{R}_\mathbf{n}')} \approx -\frac{1}{N} \sum_{\alpha=1,2} \sum_{\mathbf{n}, \mathbf{n}'} \frac{\hbar^2}{2M_\alpha} \nabla^2_{\mathbf{u}^{i\alpha}(\mathbf{R}_\mathbf{n})}, \quad (5)$$

and

$$\mathbf{V}(\mathbf{R}) = \frac{1}{N} \sum_{\alpha, n} \mathbf{V}(\mathbf{u}^{i\alpha}(\mathbf{R}_n)). \quad (6)$$

Here, in the final approximate equality of Eq. 5, we have used the fact that in evaluating the GS energy, in the semi-classical limit, odd terms involving the gradient are required to vanish.

Also, because $\mathbf{u}(\bar{\mathbf{R}}_n + \boldsymbol{\tau}_{\alpha, n} + \bar{\mathbf{L}}_j) = \mathbf{u}(\bar{\mathbf{R}}_n + \boldsymbol{\tau}_{\alpha, n})$ ($j = 1, 3$), $V(U)$ is a periodic function with respect to translations, defined by $\bar{\mathbf{L}}$. This might seem to be an artifact of the (Born VonKarman) boundary conditions. But because L is large microscopically, in the semi-classical limit, it can be macroscopically finite, and within bulk regions where the Born VonKarman boundary conditions can hold (in an approximately unambiguous manner), it follows that when, in the absence of outside perturbations, $V(U)$ is required to be periodic, by construction, any phonon wave function, technically, is also a Bloch state, associated with a new Bravais Lattice, in which each vector $\bar{\mathbf{L}}_\alpha$ is viewed as a (microscopically large) primitive vector². (In fact, for the zone center situation considered by KC, $V(U)$, by construction, is actually periodic over the smaller Bravais lattice, associated with the smallest primitive vectors, defined by $\bar{\mathbf{b}}_\alpha = \bar{\mathbf{L}}_\alpha / 2N_\alpha$.)

In the presence of the gradient terms, Ψ can be re-expressed (through an appropriate, Galilean transformation) in terms of an alternative wave function Ψ' that satisfies a modified Schroedinger equation, in which the dependence on $\nabla_{\mathbf{u}(\mathbf{R}_n + \boldsymbol{\tau}_{n, \alpha})}$ in the original equation is globally replaced with $\nabla_{\mathbf{u}(\mathbf{R}_n + \boldsymbol{\tau}_{n, \alpha}) - i\Delta\mathbf{k}(\boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n, t)}$, where $\Delta\mathbf{k}$ occurs as a result of an externally applied electric field (E). As in conventional band theory, as a function of time t , beginning from $t=0$, $\Delta\mathbf{k}(t, \boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n) = t \frac{d\mathbf{k}}{dt}$, $\hbar \frac{d\mathbf{k}}{dt} = eE$, and this perturbation can be (and is required to be, in situations where surfaces are present) non-periodic. (Here, $|e| = |\text{proton charge}|$.) Because KC modeled optical phonons, they only varied the H (D) coordinates and used the inverse of the reduced mass $1/\mu$ ($\sim 1/M_H$ or $1/M_D$, $M_H = \text{hydrogen mass}$, $M_D = \text{deuterium mass}$) in Eq. 5. Because, implicitly, their calculations are most meaningful near the equilibrium configuration, when $U=0$, without contributions from the gradient terms ($\nabla\mathbf{V}$) which are assumed to vanish.

In a finite crystal, ∇V never vanishes, but when N (=number of unit cells) is sufficiently large, usually, the resulting effects are small. In principle, an additional perturbation, V' , is always required:

$$\begin{aligned} V' &= \frac{1}{2N} \sum_{n, n', \alpha, \alpha'} \nabla_{\mathbf{r}^i} \Phi \Big|_{\mathbf{r}^i = (\mathbf{R}_n - \mathbf{R}_{n'} + \boldsymbol{\tau}_{\alpha, n} - \boldsymbol{\tau}_{\alpha', n'})^i} (\mathbf{u}^i(\mathbf{R}_n + \boldsymbol{\tau}_{\alpha, n}) - \mathbf{u}^i(\mathbf{R}_{n'} + \boldsymbol{\tau}_{\alpha', n'})) \\ &= \frac{1}{N} \sum_{n, n', \alpha, \alpha'} \nabla_{\mathbf{r}^i} \Phi \Big|_{\mathbf{r}^i = (\boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n - \boldsymbol{\tau}_{\alpha', n'} - \mathbf{R}_{n'})^i} \mathbf{u}^i(\boldsymbol{\tau}_{n, \alpha} + \mathbf{R}_n), \quad (7) \end{aligned}$$

where $-\nabla_{\mathbf{r}}\Phi = \text{force}$ (including externally applied E fields) between atoms separated by a distance r . The dependence on an effective, external E field can be introduced (as in the conventional semi-classical theory of conduction) by instantaneously transforming the reference frame that is used to solve Eq. 4 to an alternative (accelerating frame) in which the time coordinate t is multiplied by V' . Beginning from $t=0$, in the accelerating frame, instantaneously, as a function of t , the new wave function acquires momentum,

$$\frac{\hbar\Delta\mathbf{k}_i(\boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n, t)}{N} = -t \times \frac{1}{N} \sum_{n', \alpha'} \nabla_{\mathbf{r}^i} \Phi \Big|_{\mathbf{r}^i = (\boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n - \boldsymbol{\tau}_{\alpha', n'} - \mathbf{R}_{n'})^i} \quad (8)$$

The transformation to the new frame is accomplished by defining the new wave function Ψ' , using,

$$\Psi' = \mathbf{e}^{-i \sum_{i, n, \alpha} \hbar\Delta\mathbf{k}_i(\boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n, t) \mathbf{u}^i(\boldsymbol{\tau}_{\alpha, n} + \mathbf{R}_n)} \Psi \quad (9)$$

Because in a finite PdH (PdD) host, the gradient terms are present, the zone center mode $U(0)$, evaluated by KC is an approximate IBS.

3 Ion Band State Mediated Nuclear Reactions in Finite Solids

3.1 Microscopic Physics of H(D) Ion and Electron Band States

Although the semi-classical theory of electron dynamics and conduction⁶ has been widely used, it has no formal justification, based on a microscopic theory. In fact, beginning from an ordered GS, it is possible to formally justify when this treatment of conductivity applies for electrons (and ions), based on a microscopic theory, in a finite crystal. The essential physics of the associated argument is that when the GS is ordered, the lowest energy forms of reaction are initiated in bulk regions but induce heat through processes that are perfectly elastic in bulk regions, in which, effectively the momentum of the reaction is instantly transferred to the center-of-mass of the solid, as a whole (as in the response of a solid to a gamma ray in the Mossbauer effect). At higher temperatures, alternative effects, involving phonon/ion and electron band state excitations can occur, in which (ion and electron) charge, again, is transported to surface and interfacial regions.

These conclusions follow from two key features of an ordered solid, near T=0: 1.) The motion of bulk regions of the solid (which are regions in which charge is always conserved, and net changes in charge and total charge always vanish), relative to locations outside of the bulk region (in which charge is allowed to change), can never be determined without introducing some form of external perturbation; and 2.) The GS wave function of an ordered solid, in bulk regions, has minimal overlap with excited states that couple to outside forces and perturbations, involving non-bulk regions where charge imbalance is allowed to take place.

The first characteristic implies a form of symmetry: In a finite lattice, it is never possible to determine the constant zero of (kinetic) energy or momentum of the bulk region, relative to non-bulk regions, but, to determine the GS, in bulk regions, it can be assumed energy is conserved. Then, it is impossible to determine if bulk region particles are at rest or in motion.

This symmetry has important consequences: A.) Because rigid translations of the bulk uniformly shift the momentum of each bulk region particle, these kinds of translations do not alter the relative interactions between (or fluxes involving) different particles within the bulk region. B) The GS is defined in a preferred reference frame, in which the balance between outside forces defines the zero of energy and momentum, which, together, establish the energies and overlap of possible many-body states.

An important point is that the relationship between the velocity \mathbf{v} and momentum \mathbf{p} , of a charged particle, possessing charge e and mass m , is not $\mathbf{p}=\mathbf{mv}$. The precise relationship is $\mathbf{mv}=\mathbf{p}-e/c\mathbf{A}$, where \mathbf{A} (the vector potential) is defined by the magnetic field, \mathbf{B} (through the relationship $\nabla \times \mathbf{A}=\mathbf{B}$) and Maxwell's Equations. In particular, quantum mechanically, \mathbf{p} and \mathbf{A} can both change instantaneously by the same amount, even discontinuously, at any location, without changing the value of v of any particular particle. The example of a Mossbauer-like, Galilean translation, in which all particles in the bulk region are rigidly shifted, relative to an observer, further illustrates subtleties associate with the effect. In particular, since no net accumulation of charge occurs, it is impossible to determine if the bulk region is in motion or at rest. This means that in the reference frame of an outside observer who moves with velocity $-\mathbf{V}_{cm}$, the bulk region appears to move rigidly with total momentum $\mathbf{P}_{cm}=\mathbf{MV}_{cm}$ (M = mass of bulk solid), while in the frame in which both observer and bulk region are stationary, $\mathbf{P}_{cm}=0$. Because the transformation is rigid, the relationship between the wave functions $\Psi_{Bulk}(\mathbf{P}_{cm}=\mathbf{MV}_{cm})$ and $\Psi_{Bulk}(\mathbf{P}_{cm}=0)$ in the different frames involves a simple, change in phase:

$$\Psi_{bulk}(\mathbf{P}_{cm} = \mathbf{MV}_{cm}) = e^{\frac{i\mathbf{MV}_{cm} \cdot \mathbf{R}_{cm}}{\hbar}} \Psi_{bulk}(\mathbf{P}_{cm} = 0) = \prod_{i=1, N_{total}} e^{i\mathbf{k}_i \cdot \mathbf{r}_i} \Psi_{bulk}, \quad (10)$$

where $\hbar\mathbf{k}_i = \mathbf{m}_i \mathbf{V}_{cm}$ is the momentum that a neutral particle with mass m_i would have in the reference frame in which all particles move with velocity \mathbf{V}_{cm} . The subtlety occurs because near T=0 it is never possible to determine whether or not the “bulk“, as envisioned, in this last example, is in motion or at rest, or whether or not its particles really are “neutral“, quantum mechanically. This has important consequences. In particular, non-local forms of coherence can occur, in which it is possible to maintain a T=0 situation, with no interaction, whatsoever in bulk regions. This occurs when the entire bulk region moves all at once, but with different amounts of momentum (associated with different particles, as in Eq. 10).

Depending on whether the bulk is in motion or at rest, relative to non-bulk regions, wherever a particular coordinate \mathbf{r} associated with a particle of mass m , and charge e , appears in an expression involving the total many-body wave function Ψ , the expression should be multiplied by a pre-factor of the form, $\exp(i\mathbf{k} \cdot \mathbf{r})$, where $\hbar\mathbf{k}=\mathbf{mV}_{cm} + \langle e/c\mathbf{A}(\mathbf{r}) \rangle$, and $\langle e/c\mathbf{A}(\mathbf{r}) \rangle = \hbar\mathbf{k}_0 = \mathbf{p}_0$ is the average, minimum (zero) of the momentum of the particle. Here, degeneracy can occur because \mathbf{A} (as well as the value of k_0) is never uniquely defined since the gradient of an arbitrary function can always be added to \mathbf{A} , without altering the value of the magnetic field.

However, near $T=0$, it is also required that in the presence of a finite lattice, the associated forms of interaction between many-body states involve minimal, mutual overlap, in bulk regions. Thus, it follows that a discrete form of the degeneracy is involved in which, a priori, any one of the possible states, associated with a particular wave-vector, can couple to an alternative state associated with a different wave-vector, through an outside perturbation. As a consequence, through any of the possible symmetry operations (in which the bulk is translated rigidly), the value of P_{cm} associated with one such translation can only differ from the comparable momentum of a second translation by the product of \hbar and one of the wave-vectors within the First Brillouin Zone (defined by Born VonKarman boundary conditions of the finite crystal). This result follows by considering the potential forms of interaction between the GS and possible, low-lying forms of excited states.

In particular, as a function of time t , the requirement that the lowest energy (GS) many-body wave function $\Psi_{GS}(\mathbf{r}_1, \dots, \mathbf{r}_n, t)$ have minimal coupling with outside processes, means that its overlap with any other many-body state $\Psi'(\mathbf{r}_1, \dots, \mathbf{r}_n, t)$ be minimized and remain constant. A requirement for this to occur is:

$$\frac{\partial \langle \Psi' / \Psi_{GS} \rangle}{\partial t} = \iiint d^3 r_1 \dots d^3 r_n \frac{\partial (\Psi'^* \Psi_{GS})}{\partial t} = - \int d^3 r \nabla \cdot \langle \Psi' / v(r) / \Psi_{GS} \rangle + \langle \Psi' / \frac{V - V'}{\hbar} / \Psi_{GS} \rangle = 0, \quad (11)$$

where terms in the second equality are defined by the many-body Schroedinger equations of Ψ' and Ψ_{GS} .

In general, the associated integrations are unrestricted. To minimize overlap in "bulk regions", unrestricted integrations over all of the coordinates in the multi-dimensional integral, term by term, can be restricted to regions in the bulk, based on the criteria that to find a possible GS, the associated overlap between this state and other states in the bulk region be minimized. In this limited context, by restricting states to have minimal overlap with Ψ_{GS} , additional restrictions are imposed on Ψ_{GS} (subject to the additional, implicit assumption that, in general, at the boundaries of the bulk region, possible discontinuities in the gradient and vector potential, are allowed to take place). Then, the associated analysis proceeds by restricting the multi-dimensional integrations in Eq. 11, exclusively to the bulk region. Also, in Eq. 11, $\langle \Psi' | v(r) | \Psi_{GS} \rangle$ is the matrix element associated with the (off-diagonal) contribution to the (many-body) particle velocity operator v , defined by its overlap with the states Ψ' and Ψ_{GS} :

$$\langle \Psi' | v(r) / \Psi_{GS} \rangle = \sum_j \iiint d^3 r_1 \dots d^3 r_n \delta^3(r - r_j) \frac{1}{m_j} \left(\frac{\hbar}{2i} [\Psi'^* \nabla_{r_j} \Psi_{GS} - \nabla_{r_j} \Psi'^* \Psi_{GS}] - \frac{e_j}{c} \Psi'^* A_{eff}(r_j) \Psi_{GS} \right), \quad (12)$$

where $A_{eff}(r) = (A(r) + A'(r))/2$ is the arithmetic mean between the vector potential $A'(r)$ associated with the state Ψ' and the comparable vector potential $A(r)$, associated with the state Ψ_{GS} , and the final term in Eq. 11 is defined by the difference between the many-body potential energy associated with states Ψ' and Ψ . In particular, this last term, is given by

$$\langle \Psi' | \frac{V - V'}{\hbar} | \Psi_{GS} \rangle = \langle \Psi' | \frac{V_{em} - V'_{em}}{\hbar} | \Psi_{GS} \rangle + \langle \Psi' | \frac{V_s - V'_s}{\hbar} | \Psi_{GS} \rangle, \quad (13)$$

where $\langle \Psi' | V_{em} - V'_{em} | \Psi_{GS} \rangle$ is the difference in electromagnetic potentials associated with coupling between the vector potentials $A'(r)$ and $A(r)$,

$$\langle \Psi' | V_{em} - V'_{em} | \Psi_{GS} \rangle = \int d^3 r \frac{(\mathbf{A}(r) - \mathbf{A}'(r)) \cdot \mathbf{J}(r)}{c}, \quad (14)$$

defined by the associated current $\mathbf{J}(r)$,

$$\langle \Psi' | \mathbf{J}(r) / \Psi_{GS} \rangle = \sum_j \iiint d^3 r_1 \dots d^3 r_n \delta^3(r - r_j) \frac{e_j}{m_j} \left(\frac{\hbar}{2i} [\Psi'^* \nabla_{r_j} \Psi_{GS} - \nabla_{r_j} \Psi'^* \Psi_{GS}] - \frac{e_j}{c} \Psi'^* A_{eff}(r_j) \Psi_{GS} \right),$$

and (in Eq. 13), the remaining contribution to the difference in potential energy is defined by any change in electrostatic or other (including nuclear) contribution to the energy, associated with the transition from Ψ' (where the non-electro-dynamic portion of the potential energy is V_s') to Ψ_{GS} (which has a corresponding non-electro-dynamic potential energy V_s).

Eq. 11 vanishes identically whenever the energies associated with Ψ_{GS} and Ψ' are the same. When Ψ_{GS} has minimal coupling to the bulk, Eq. 11 holds identically, outside the bulk, provided all of the external forces vanish and the total internal flux of all particles into and away from the bulk region also vanishes. Thus, if the flux of particles, across all boundaries in the bulk vanishes, and the energies of the different states are the same within the bulk region, it follows from Eq. 11,

$$\int \mathbf{d}^3\mathbf{r} \nabla \cdot \langle \Psi' | \mathbf{v}(\mathbf{r}) | \Psi_{\text{GS}} \rangle = \int_{\partial V} \mathbf{dS} \hat{\mathbf{n}} \cdot \langle \Psi' | \mathbf{v}(\mathbf{r}) | \Psi_{\text{GS}} \rangle = \frac{i}{\hbar} \iiint_V \mathbf{d}^3\mathbf{r}_1 \dots \mathbf{d}^3\mathbf{r}_n \Psi'^* (\mathbf{V} - \mathbf{V}') \Psi = 0, \quad (15)$$

where the integration in the final term extends over the bulk region, and the surface integral (associated with $\mathbf{v}(\mathbf{r})$) extends over the boundary of the bulk region. In principle, although this surface integral includes separate contributions from regions where \mathbf{v} may become discontinuous (which are allowed to occur whenever $\mathbf{V} - \mathbf{V}'$ becomes singular), for the purpose of identifying the GS, Ψ_{GS} and Ψ' can be selected in such a way that $\mathbf{V} - \mathbf{V}'$ is never singular. Then, a necessary and sufficient condition to guarantee that the left side of Eq. 2 vanishes within some volume, defined by a set of boundary planes, in which each point \mathbf{r} on one boundary plane is related to a point \mathbf{r}' on a second boundary plane, by one of the three vectors, $\bar{\mathbf{L}}_\alpha$, is that

$$\mathbf{v}(\mathbf{r} + \bar{\mathbf{L}}_\alpha) = \mathbf{v}(\mathbf{r}') = \mathbf{v}(\mathbf{r}). \quad (16)$$

In the limit in which, Ψ' and Ψ_{GS} are identically the same in the bulk region (but are allowed to be different outside the bulk), and A_{eff} equals a constant, Eq. 16 holds if and only if for each coordinate r_i ,

$$|\Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_i + \bar{\mathbf{L}}_\alpha, \dots, \mathbf{r}_n)|^2 = |\Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)|^2, \quad (17)$$

and

$$\frac{\partial \ln \Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_i + \bar{\mathbf{L}}_\alpha, \dots, \mathbf{r}_n)}{\partial r_i^m} = \frac{\partial \ln \Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n)}{\partial r_i^m}, \quad (18)$$

where r_i^m is the x, y or z component (for $m=1,2, \text{ or } 3$) of the coordinate \mathbf{r}_i . The general solution of Eqs. 17 and 18 is

$$\Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_i + \bar{\mathbf{L}}_\alpha, \dots, \mathbf{r}_n) = \lambda_i \Psi_{\text{GS}}(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n), \quad |\lambda_i| = 1. \quad (19)$$

Eq. 19, is a generalization of Bloch's theorem, for finite lattices that holds, whenever it is possible to define boundaries through the three vectors, $\bar{\mathbf{L}}_\alpha$, for a GS that obeys Eq. 15. In particular, when Eq. 19 holds over distances that are smaller (by a factor of $2N_\alpha$), it also holds when the smaller primitive vectors \mathbf{b}_α are used.

When $\mathbf{b}_\alpha = \frac{\bar{\mathbf{L}}_\alpha}{2N_\alpha}$, it follows from Eq. 19 that

$$\lambda_i(\bar{\mathbf{L}}_\alpha) = \lambda_i(2N_\alpha \mathbf{b}_\alpha) = \lambda_i(\mathbf{b}_\alpha)^{2N_\alpha}. \quad (20)$$

In general, the R.S. of Eq. 14 does not vanish. But when Ψ' satisfies an alternative version of Eq. 19, in which λ_i is replaced with a different eigenvalue λ_i' , even when A does not equal A' , provided A and A' are periodic functions, with respect to Bravais translations, defined by \mathbf{b}_α , it follows that

$$\ln\left(\frac{\lambda_i(\mathbf{b}_\alpha)}{\lambda_i'(\mathbf{b}_\alpha)}\right) = i \frac{\pi \mathbf{n}}{N_\alpha} = i \mathbf{k} \cdot \mathbf{b}_\alpha, \quad (21)$$

where n is an integer, and \mathbf{k} is one of the discrete vectors defined by the finite lattice. Since $|\lambda_i| = |\lambda_i'| = 1$, it follows that both Ψ' and Ψ_{GS} can be written using a common functional form Ψ , in which the dependence on changes in the phase associated with either eigenvalue (as in Eq. 21) occur through a plane-wave that changes as any of the coordinates is displaced by a Bravais vector \mathbf{R}_n , and through a second function u that is periodic with respect to translations of any of its coordinates by \mathbf{R}_n ; i.e. for $\Psi = \Psi'$ or $\Psi = \Psi_{\text{GS}}$, Ψ can be written as

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) = e^{i \sum_j \mathbf{k}_j \cdot \mathbf{r}_j} u(\mathbf{r}_1, \dots, \mathbf{r}_n), \quad (22)$$

where $\mathbf{u}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \mathbf{u}(\mathbf{r}_1, \dots, \mathbf{r}_i + \mathbf{R}_n, \dots, \mathbf{r}_n)$ for coordinates \mathbf{r}_i . Because Ψ_{GS} or Ψ' can be written using Eq. 22, the gradient of $\mathbf{k}_i \cdot \mathbf{r}_i$ in the exponential factor simply alters the value of A or A' through a (trivial) gauge transformation (associated with changing the value of \mathbf{p}_0), for each particle in the many-body Schroedinger equation of the one state (associated with $\mathbf{V}_s = \mathbf{V}_s'$) that differs from the other only through a change in \mathbf{p}_0 . Thus, a large degree of symmetry exists, in which one, two, ..., n , Bravais translations, in principle could be performed, in which the energy is not changed, while the value of \mathbf{p}_0 associated with the coordinate of one (or more) particles is shifted relative to another. (This is the origin of the generalized, double Bloch symmetry that we have previously

used⁷.) In fact, outside forces constrain the lattice and break the associated degeneracy. As alluded to above, the lowest energy processes involve situations, in which, in the bulk region, the state describes a configuration of particles that is neutral (on the average, in each unit cell), and in which all particles move with a common, velocity V_{cm} . In this limit, $\sum_i \mathbf{k}_i \cdot \mathbf{r}_i = \frac{\mathbf{V}_{cm}}{\hbar} \sum_i \mathbf{m}_i \cdot \mathbf{r}_i = \frac{\mathbf{M}\mathbf{V}_{cm} \cdot \mathbf{R}_{cm}}{\hbar}$, and the vector potential for each charged particle is measured relative to its constant zero of momentum.

In practice, determining \mathbf{p}_0 for the GS (and low-lying excited states) for each charged particle is formidable on a microscopic scale in finite crystals because as charge begins to accumulate, potentially large variations in electric field and charge density can occur. For this reason, in general, it is impossible to identify GS properties based on the kind of (simpler) rules that apply in bulk crystals, and calculations that include specific information about non-bulk regions (near surfaces or interfaces) are required. But in larger crystals, asymptotically, it is possible to understand, at least in an average sense, how by averaging many terms, a number of important approximate aspects of the associated coupling can occur in most crystals. The resulting perturbations break the degeneracy of the lowest energy states in the “bulk solid” by fixing the value of \mathbf{p}_0 associated with each particle of each state, relative to the comparable zero of momentum of every other particle, in every other state. This requirement, also fixes the value of the zero of energy ε as a function of \mathbf{p}_0 ; i.e. $\varepsilon = \varepsilon(\mathbf{p}_0)$ for each particle and state relative to the electrostatic zero and physical vector potential that are present in the solid. The resulting values of $\varepsilon(\mathbf{p}_0)$ define the lowest lying energy band states.

By requiring that $\langle \Psi_{GS} | \Psi_{GS} \rangle$ be constant and stable with respect to infinitesimal variations in each value of \mathbf{p}_0 , it is possible to derive a generalization of the semi-classical dynamics and transport theory of charged (band state) particles (electrons and ions). Here, provided externally applied forces F and charge vary sufficiently slowly in the external regions, the gradient of each value of $\varepsilon(\mathbf{p}_0)$ with respect to \mathbf{p}_0 , for a particular particle, identically equals the expectation value of its velocity operator v , averaged over the bulk and surface regions. Also, provided F varies sufficiently slowly, the associated changes in \mathbf{p}_0 , obey $\Delta \mathbf{p}_0 = \int \mathbf{F} dt$. Thus, a change in wave-vector $\Delta k = \Delta p / \hbar$, as a function of time, that is conventionally associated with each band energy in the semi-classical theory⁶, can rigorously be interpreted as a shift in the zero of momentum of each state. Details about this are discussed in the Appendix and elsewhere⁸.

3.2 Nuts and Bolts of Ion Band State Nuclear Reactions in Solids

Previously, we suggested[7-9] when the separation between two charged particles r_{ij} ($= r_i - r_j$) approaches zero, overlap can still occur if the wave function has “cusps” at these locations. This argument addresses the Coulomb barrier penetration problem but only qualitatively because it involves assumptions about the cusps. Also, the argument does not explain momentum transfer to the solid, and energy release.

The argument can be generalized (because it is a limiting case of Eq.15) by replacing Ψ_{GS} with an arbitrary state Ψ_0 . Then, provided Ψ_0 and Ψ' have the same energy, formally, Eq. 15 can be used to define the contribution T_{f_0} to the transition matrix element, associated with a transition between Ψ_0 and $\Psi' = \Psi_f$. (The subscript in each state refers to all quantum numbers.) When each integration is extended throughout space, it follows from the Lippmann-Schwinger Equation that the rate $R_{0 \rightarrow f}$ associated with the transition from Ψ_0 (possessing initial state energy E_0) to Ψ_f (possessing energy E_f) is given by $R_{0 \rightarrow f} = \frac{2\pi}{\hbar} \delta(E_f - E_0) |T_{f_0}|^2$, and the total reaction rate R_T is given by

$$R_T = \sum_f R_{0 \rightarrow f} \cdot (23)$$

Instead of dealing with Eq. 23, directly, the earlier treatment⁷ dealt with a simpler (related) problem: requiring that the bulk region remain in its GS, during the nuclear reaction. In particular, to remain in its GS, in the bulk: 1. No accumulation of charge (per unit cell) occurs; 2. All particle flux (in Eq. 15) vanishes (into and away from the bulk), including flux from the surface region and nuclear active reactions (NAR's), near the location(s) where d+d overlap can occur. (Implicitly, to use Eq. 15 to identify properties of the GS, particle fluxes from the NAR's, defined by a collection of infinitesimally small volumes, centered about each location where overlap on a nuclear scale can also occur, are excluded because reactions in these regions can alter both p_0 and the charge in the bulk.) Instead, in the earlier treatment⁷, at each location in the NAR, an approximate boundary condition (through a wave function cusp) was imposed.

In the more general problem associated with Eq. 23, the earlier limit⁷ occurs when the bulk region remains in its GS, and the variational calculation⁷ is equivalent to minimizing R_T , with no net particle flux into the bulk, and contributions to R_T occurring only from discontinuous changes in momentum at all boundaries (which are introduced, effectively, through boundary conditions, involving the cusps). Eq. 23, in the extreme low T limit, justifies this picture. Then, no interaction occurs in the bulk, and ${}^4\text{He}$ is produced in IBS form^{7,9} but, technically, in regions external to the bulk (in the NAR, at locations where d+d overlap can occur), and the associated change in mass is converted into momentum that is transferred through perfectly elastic (Mossbauer-like) UmKlapp processes in which bulk region moves rigidly, and heating occurs through excitation from interaction involving residual ${}^4\text{He}$ that is released in surface regions, where lattice heating is initiated. Thus, the entire solid acquires a fixed

(common) velocity V_{cm} , defined by $V_{\text{cm}} = \frac{\Delta P}{M}$, where $M (= N \times (M_{\text{Pd}} + M_{\text{D}}))$, M_{D} =mass of D-atom, M_{Pd} =Pd

mass) is the total mass of the bulk, and $\Delta P (= \sqrt{Q2M_{\text{He}}})$, $Q=23.8$ MeV) is the available momentum (from

$d+d \rightarrow {}^4\text{He}$), and because all the particles have velocity V_{cm} , the shift in \mathbf{p}_0 from the cusps, resulting from ${}^4\text{He}$

occupying IBS's is $M_{\text{He}} V_{\text{cm}} = \frac{M_{\text{He}} \Delta P}{M_{\text{total}}}$.

A natural generalization of the earlier model⁹ exists, in which to conserve momentum, this shift in \mathbf{p}_0 results in a physical change in \mathbf{p}_0 for the entire solid, as a whole (through the rigid shift). In particular, this shift in \mathbf{p}_0 occurs through the dependence of the many-body wave function on the separation variable r_{ij} . The requirement that the shift occur rigidly is that $\Delta P_{\text{cusp}}=G$, where G is a reciprocal lattice vector². But again (consistent with the

model), for the bulk to remain in its GS, the magnitude of $\Delta P_{\text{cusp}} \sim M_{\text{He}} V_{\text{cm}}$. Using this last inequality, the

previous equality, and a suitable (minimal magnitude) value for $G (= \frac{2\pi\hbar}{a_{\text{PdD}}})$; a_{PdD} =Pd-Pd separation in

$\text{PdD} \approx 2.89 \text{ \AA}$) it is possible to establish a lower bound for N (=number of unit cells):

$$\frac{\sqrt{2QM_{\text{He}} M_{\text{He}} a_{\text{PdD}}}}{(M_{\text{Pd}} + M_{\text{D}})2\pi\hbar} \approx 3000 \leq N. \quad (25)$$

This bound for N holds at $T=0$, provided no outside sources of momentum dissipation or enhancement are present. In general, at finite T , many alternative forms of reaction are present. A detailed computational scheme does exist⁹ for addressing this kind of problem. Further extensions of this kind of approach can be applied. Detailed work in this area probably will be carried out in the future.

4 Appendix: Semi-Classical Dynamics of Ion and Electron Band States in Finite Crystals

The Semi-Classical Equations of Motion that have been used to describe the dynamics of electrons in solids have never been formally justified. An important reason for this is that these equations do not hold in general. However, using the results of section 3.1, it is possible to generalize these equations, formally, and explain how as a solid becomes sufficiently large, asymptotically, these equations can be required to be valid both for electrons and hydrogen ions, in the limit of vanishing T . The central physics involves appropriately incorporating external forces.

In larger crystals, the relevant dynamics approximately follows from averaging many terms, either on the R.S. or left-side (L.S.) of Eq. 11. This is possible when Gauss's law applies. Then, characteristic changes in the electric field can, in principle, be used to identify trends associated with approximate effects involving charge distribution, which, in turn, can be used to determine asymptotic limits and average values of many of the terms in Eq.11. In particular, the idealized limit in which periodic order is disrupted only in directions normal to an interface (or surface) region can be used to illustrate how changes in a boundary can alter the conventional (bulk) picture (associated with energy bands, in an infinitely repeating, periodic solid) that can justify why (and when) the Semi-Classical Equations of Motion for describing the dynamics of bulk charges that occupy band states can be used to describe the conduction of charge (and other transport phenomena) in solids, in the presence of boundaries.

In particular, in this idealized limit, the generalized form of Bloch's theorem (Eq. 19) can apply in directions parallel to the crystal surface (or interface). But for this case, asymptotically, in directions normal to the surface, but sufficiently far away, both the electrostatic potential and electric field are required to exponentially decay (on the average). When the induced redistribution in charge associated with any applied field scales in a linear manner (which occurs universally in metals, and in Pd, in particular), exponential decay in induced charge and its charge density also occur. The resulting coupling leads to finite overlap between states possessing different wave-vectors in the normal direction but preserves periodic symmetry in directions parallel to the surface. In practice, this means that in directions normal to the surface, the values of the momentum (and wave-vector) acquire an imaginary component. The associated perturbations break the degeneracy of the lowest energy states in the bulk solid by constraining the value of the local zero of momentum p_j associated with the local value of the vector potential A of a particular particle of a particular state, with respect to a particular coordinate r_j , relative to the average zero of momentum p_o . This requirement, as a consequence, fixes the value of any external vector potential A , at all points in the solid, and the requirement can also define how each particle in the bulk region can interact with the electromagnetic field.

As a consequence, once the zero of momentum, p_o , of the solid (as a whole) is fixed, all states, associated with symmetries that are allowed in Eq. 19 can become possible (as opposed to a situation in which a more limited subset of states, associated with Eq. 10, are allowed). In particular, in the most general situation, $\mathbf{p}_o = \sum_j \mathbf{p}_j$,

where p_j is the minimum value of momentum (which we will refer to as the local zero of momentum) associated with the dependence of Ψ_{GS} on the coordinate r_j , that asymptotically (as discussed below) can be related to a particular particle or (in situations involving correlation) a collection of particles. Each value of p_j , in turn, is fixed by the average variation in $A(r_j)$ that can result from its overlap with Ψ_{GS} with respect to this coordinate.

Consistent with the requirement that changes in p_j also preserve particle exchange symmetry, p_j is required to be the same for each indistinguishable particle of a particular kind. But different kinds of particles can (and usually will) have different values of p_j . In particular, extreme situations can occur, in which through particle exchange symmetry, counter-intuitive forms of coupling can occur (including Bose-Einstein Condensation) through energy minimization.

Classically, the lowest value of the energy (which is a convenient definition of the zero of energy) of a particle that possesses mass m and velocity v occurs, locally, when $v=0$ (so that $\frac{1}{2}mv^2=0$). Quantum Mechanically, the same definition can also be used within particular regions of space, but in the presence of boundaries, and when indistinguishable particles are present, non-local forms of coupling can occur. As a consequence, in general, every coordinate in Ψ_{GS} should be treated as having a separate zero of energy V_j . In practice, because each value of V_j is defined (using Eq. 12 through matching conditions) by momentum conservation at the boundaries of the bulk, the problem of determining V_j in the bulk is equivalent to the problem of solving an equivalent minimization problem (which is frequently expressed in terms of a well-defined Rayleigh-Ritz variational procedure) for each eigenvalue ϵ_j (which can be defined as a generalized form of band state energy) associated with the many-body Schroedinger equation. In particular, to determine the GS, it is possible (and consistent with energy minimization) to define each value of V_j , using, $V_j=\epsilon_j$, and to require that $E_{GS} = \sum_j \epsilon_j$.

The problem of solving the associated many-body Schroedinger Equation for each value of ϵ_j requires detailed information about the fluxes of particles at the boundaries of the bulk region as well as additional information (in situations in which correlation is present) associated with particle exchange symmetry, including effects involving the possible exchange of internal quantum numbers (such as magnetic spin). Because of the wide variability of boundary conditions that can be imposed, it is not possible, in general, to solve this particular problem uniquely without imposing particular restrictions on the behavior of Ψ_{GS} in non-bulk regions. But it is possible to use approximate boundary conditions associated with the relevant dynamics in order to understand a number of key features associated with the relevant effects.

In particular, considerable progress can be made by requiring that the functional form of the most general many-body wave function that is used to describe the GS (or in the comparable wave function that describes the low-lying excited states) asymptotically approach the functional form that applies in the independent particle limit in non-bulk regions either at the boundaries of the bulk or (provided additional constraints are imposed) far from the boundaries of the bulk region. In particular, well-defined effects can be used to understand the behavior of the associated state in this asymptotic limit, immediately at the boundaries of the bulk region or far from the boundary

(provided the wave function asymptotically approaches the associated functional form far from the boundaries and is non-vanishing and continuously differentiable between the boundary and the location far from the boundary where this functional form applies). When this limit applies, specifically, either at the boundary, asymptotically far from the boundaries of the bulk region, or at intermediate locations, in non-bulk regions, functional forms associated with Ψ_{GS} and more general functional forms that apply for wave functions Ψ (that describe low-lying excited states of the bulk) can be expressed using sums of products of single particle wave functions, describing fermions and bosons. Then, in these regions, each fermion (boson) wave function can be expressed using an anti-symmetrized (symmetrized) sum of products of single particle wave functions.

The significance associated with the possibility that this limit might apply is that when it applies, it is possible to identify and order the associated eigenvalues ε , using the (conventional) nomenclature (associated with “occupied” and “unoccupied” states) that applies in the independent, single particle picture, associated with conventional band theory. As a consequence, values of ε associated with “occupied states” (in Ψ_{GS}) can be distinguished from “unoccupied states” (that occur in the wave functions Ψ) that describe the low-lying excited states of the bulk.

This point is significant because consistent with the requirement that changes in p_j also occur (from symmetries involving particle exchange) through indistinguishable particles, counterintuitive relationships can occur (associated with energy minimization) in which changes in flux (in Eq. 12) can be enhanced or be impeded by effects associated with fermion or boson occupation. These effects, which involve changes in $\mathbf{A}(\mathbf{r}_j)$ that result from changes in \mathbf{p}_j , can lead to particular forms of coupling that do (and are required to) occur. As a consequence, the associated energy minimization procedure is constrained so that the total (ground state) flux of each particle (in Eq.15) vanish when the integrations (in Eq. 15) are extended throughout the solid and that this flux be stable with respect to any infinitesimal variation in \mathbf{p}_j and the changes in the zero of energy associated with this form of variation. Because exchange symmetry does not alter the internal dynamics, it is possible to introduce the associated effects by selecting the “global” zero of energy in an appropriate way for each particle. This can be done either directly (for bosons, including d’s or ^4He nuclei) or indirectly (for fermions, including p’s and electrons). In particular, the value of the global zero can be equated with the lowest (for bosons) or highest (for fermions) value of the local zero of energy (i.e., the lowest or highest occupied band state eigenvalue ε), defined, asymptotically, by the non-bulk region (independent particle) wave function. Thus, in either (the fermion or boson) case, a single, independent, value of ε can be used to determine the behavior of the GS and lowest states of excitation, based on a relative state of motion, defined by the relative momentum between the bulk and non-bulk regions. In particular, in a reference frame that has momentum $\mathbf{p}_j \equiv \hbar \mathbf{k}_j$, relative to a frame that is stationary, the local zero of energy (associated with a particular band state eigenvalue, ε) can be defined by the value of the local zero of the (highest or lowest occupied) energy of a single particle energy state $\varepsilon (= \varepsilon(\mathbf{k}_j))$, associated with possible forms of interaction that can lead to excitations of the GS.

For this reason, in either case (for fermions or bosons), the average zero of energy can be defined relative to the lowest –lying states of excitation, using a single value of the energy (which at $T=0$ can be equated with the chemical potential). By requiring that no changes occur in the bulk region, relative to non-bulk regions, all energies and changes in relative momentum between particles are fixed, with respect to the possibility that the solid (as a whole), as in Eq. 10, be allowed to move rigidly. By imposing the effects of such rigid forms of motion on the associated dynamics, it is possible to identify the lowest energy forms of response, involving the bulk region, with respect to outside perturbations (and forces). For this reason, the identification of the zero of momentum and its evolution in response to external forces can be used to identify and introduce dynamical changes in the bulk region. In particular, as a consequence, because it is impossible to determine absolutely whether or not the bulk region as a whole, is in motion or at rest, with respect to non-bulk regions, each value of the local zero in wave vector \mathbf{k}_j can be used to define the lowest lying excitations of the solid. For the same reason, the stability of the solid with respect to variations involving \mathbf{k}_j can be used to define variations in the position and momentum of the bulk region (associated with displacements that do not alter the internal energy of the bulk) relative to non-bulk regions. As a consequence,

relative to the local wave-vector $\mathbf{k}_j \equiv \frac{\mathbf{p}_j}{\hbar}$ (associated with the local zero of energy, defined by the band state, $\varepsilon = \varepsilon(\mathbf{k}_j)$, in a particular frame), within the bulk region, to determine the GS it is required that: 1. The absolute zero (defined by $\langle \Psi_{GS} | E_{GS} - H | \Psi_{GS} \rangle = 0$) of the energy be independently stable with respect to variations of each eigenvalue, $\varepsilon(\mathbf{k}_j)$, and 2. The ground state flux in Eq. 15 (defined by $\Psi' = \Psi_{GS}$) vanish and be stable with respect to

any infinitesimal change in any value of \mathbf{k}_j (and shift in zero of energy $\varepsilon(\mathbf{k}_j)$) associated with each coordinate in Ψ_{GS} , relative to its initial value. The first requirement (involving the stability of the absolute zero) is satisfied when

$$(E_{GS} - H) \frac{\partial \Psi_{GS}}{\partial \varepsilon(\mathbf{k}_j)} = \Psi_{GS}. \quad (A1)$$

(Here, $\frac{\partial \Psi_{GS}}{\partial \varepsilon(\mathbf{k}_j)}$ is defined using perturbation theory, through an infinitesimal change in the effective zero of energy, $\varepsilon(\mathbf{k}_j)$.) The second requirement is satisfied when

$$\iiint d^3n \mathbf{r} \left(\frac{\partial \Psi_{GS}^*}{\partial \mathbf{k}_j} (E_{GS} - H) \Psi_{GS} + \Psi_{GS}^* (E_{GS} - H) \frac{\partial \Psi_{GS}}{\partial \mathbf{k}_j} \right) = 0, \quad (A2)$$

where $\frac{\partial \Psi_{GS}}{\partial \mathbf{k}_j}$ is the gradient of Ψ_{GS} with respect to the wave vector $\mathbf{k}_j = \frac{\bar{\mathbf{p}}_j}{\hbar}$ associated with the coordinate \mathbf{r}_j

that is used to define the position of each particle. Here, the variation with respect to \mathbf{k}_j includes the dependence of Ψ_{GS} on implicit effects that result from changes in the zero of energy, and on explicit changes that occur when the momentum \mathbf{p}_j of each individual particle is separately varied. (In particular, by rigidly shifting the zero of this value of momentum, implicit forms of dependence occur, for example, in the plane-wave, phase factor that results from the Galilean transformation in Eq. 10 and related, alternative, approximately coherent, forms of motion.)

Specifically, here, the dependence on \mathbf{k}_j is treated implicitly through the change in the zero of energy that is used to define the periodic function, u (in Eq. 22), and explicitly through the dependence on \mathbf{k}_j that appears in the associated plane-wave factor (also in Eq. 22). In particular, in the periodic function u , each coordinate \mathbf{r}_j , by construction, has associated with it an implicit dependence on the zero of energy, through the eigenvalue $\varepsilon(\mathbf{k}_j)$, that varies as the wave-vector, \mathbf{k}_j , is changed. Although in a finite lattice, the spectrum of possible eigenvalues $\varepsilon(\mathbf{k}_j)$ is discrete, because these values are fixed by breaking a continuous symmetry (associated with allowing the lattice to rigidly shift over a continuum of possible momentum values), the gradient $(\frac{\partial \varepsilon(\mathbf{k}_j)}{\partial \mathbf{k}_j})$ of each eigenvalue, with respect to changes in wave-vector \mathbf{k}_j is well-defined. Also, in principle, the explicit dependence of Ψ on \mathbf{k}_j (through the phase factor) can become quite complicated through direct and indirect forms of coupling to the electromagnetic (EM) field.

On the other hand, since the GS is required to have minimal coupling to outside processes, coupling between indistinguishable particles is distinctly different from the comparable coupling between particles that are distinguishable. Thus, it is possible to assign a preferential gauge (and zero of momentum) to each (indistinguishable) fermion or boson, subject to the requirement that Bose-Einstein (BE) or Fermi-Dirac (FD) statistics apply in an appropriate manner. In unusual circumstances, coupling to the EM field also can occur through effects associated with spin (and other internal states) that can alter the normal exchange properties (with respect to coordinates \mathbf{r}_j associated with position) of fermions and bosons. (These effects, in particular, can become dominant in the asymptotic limit, involving vanishing T , without external forces.) For this reason, the manner in which variations in the zero of momentum are required to be consistent with BE or FD statistics is intimately related to the way the system is prepared.

But in most situations, the limit that applies at low T occurs when system momentum and energy are minimized and minimal (maximal) occupation of momentum states by fermions (bosons) takes place. In principle, as a consequence, it is possible that when exotic forms of interaction are present, situations can occur (involving fermions) in which a common value of \mathbf{k}_j can appear as a pre-factor of many different coordinates (\mathbf{r}_j) in the phase factor in Eq. 22. But this kind of situation occurs infrequently. Thus, in most situations, when fermions are involved, it is possible to assign a single value of \mathbf{k}_j to a single coordinate \mathbf{r}_j ; while in the case of bosons (including situations that occur in superconductors, where even numbers of fermions become paired), because of particle exchange and coupling to internal quantum states, situations can occur involving many particles that can possess different coordinates \mathbf{r}_i , and a common wave-vector, \mathbf{k}_j . In general, to understand how potential coupling to a common wave-vector \mathbf{k}_j can occur, for each set (or, potentially, subset) of indistinguishable particles, it is appropriate to identify a set $\{j\}$ of different coordinates ($\{\mathbf{r}_{j'}\}$) and momenta ($\{\mathbf{p}_{j'} = \hbar \mathbf{k}_{j'}\}$) of indistinguishable particles that can have a common wave-vector $\mathbf{k}_j (= \mathbf{k}_i, i \in \{j'\})$. Using this fact, it is possible

to write the resulting variation in Ψ_{GS} with respect to changes \mathbf{k}_j both implicitly (through $\frac{\partial \varepsilon(\mathbf{k}_j)}{\partial \mathbf{k}_j}$) and explicitly (through the phase factor), using

$$\frac{\partial \Psi_{GS}}{\partial \mathbf{k}_j} = \sum_{\{j'\}} \frac{\partial \Psi_{GS}}{\partial \varepsilon_{j'}(\mathbf{k}_j)} \frac{\partial \varepsilon_{j'}(\mathbf{k}_j)}{\partial \mathbf{k}_j} + i \sum_{\{j'\}} \mathbf{r}_{j'} \Psi_{GS}. \quad (A3)$$

Here, in the first term, a separate subscript (j') is used for each eigenvalue, $\varepsilon(\mathbf{k}_j)$ ($\equiv \varepsilon_{j'}(\mathbf{k}_j)$), in order to account for the possible change in the zero of energy ($\Delta \varepsilon_{j'}(\mathbf{k}_j)$) that can occur in each coordinate ($\mathbf{r}_{j'}$) of Ψ_{GS} , and the separate summations in both terms extend over values of j' associated with coordinates $\mathbf{r}_{j'}$ in Ψ_{GS} where (within the phase factor in Eq. 22) a common wave-vector \mathbf{k}_j is used. Also, the number of independent wave-vector (\mathbf{k}_j) values is $2N$ (since \mathbf{k}_j is in the First Brillouin Zone).

To identify either the GS or the lowest lying excitations of the GS, Eq. A3 must hold asymptotically for individual terms associated with different values of j' , so that individual terms, associated with variations of Ψ_{GS} with respect to its dependence with respect to a particular value of j' (through $\varepsilon_{j'}(\mathbf{k}_j)$ and $\mathbf{r}_{j'}$) can be treated as being independent from comparable variations involving a different value of j' . Then, for fermions, or for bosons, individual contributions for each band (associated with the index j') can be identified. As a consequence, using Eqs. A1-A3, it follows that it is possible to relate the average value of the velocity of any of the (indistinguishable) particles associated with all coordinates \mathbf{r}_j that possess wave-vector \mathbf{k}_j to the variation in band energy using,

$$N_{F,B}(\mathbf{k}_j) \frac{\partial \varepsilon_{j'}(\mathbf{k}_j)}{\partial \mathbf{k}_j} = \frac{1}{m_j} \frac{\iiint d^3 \mathbf{r} \left[\frac{\hbar}{2i} \left(\Psi_{GS}^* \frac{\partial \Psi_{GS}}{\partial \mathbf{r}_{j'}} - \frac{\partial \Psi_{GS}^*}{\partial \mathbf{r}_{j'}} \Psi_{GS} \right) - \frac{e_j \Psi_{GS}^* A(\mathbf{r}_{j'}) \Psi_{GS}}{c} \right] N_{F,B}(\mathbf{k}_j)}{\iiint d^3 \mathbf{r} \Psi_{GS}^* \Psi_{GS}}, \quad (A4a)$$

where $N_{F,B}(\mathbf{k}_j) \equiv \mathbf{n}_{\mathbf{k}_j} = 0, 1$ or 2 for fermions (depending on whether or not $0, 1$ or 2 spins occupy the band), and for bosons, $N_{F,B}(\mathbf{k}_j) = 0$, or N_B , where N_B = number of bosons. In either case, since a common factor of $N_{F,B}(\mathbf{k}_j)$ appears on both sides of Eq. A4a, in the independent particle limit (as in conventional band theory), in which Ψ_{GS} can be written in non-bulk regions, in terms of a sum of (suitably) symmetrized (or anti-symmetrized) products of individual wave functions $\phi_{d(k)}$, it follows that

$$\frac{\partial \varepsilon_{j'}(\mathbf{k}_j)}{\hbar \partial \mathbf{k}_j} \equiv \frac{1}{m_j} \frac{\iiint d^3 \mathbf{r}_j \left[\frac{\hbar}{2i} \left(\phi_{\mathbf{r}_j(\mathbf{k}_j)}^* \frac{\partial \phi_{\mathbf{r}_j(\mathbf{k}_j)}}{\partial \mathbf{r}_{j'}} - \frac{\partial \phi_{\mathbf{r}_j(\mathbf{k}_j)}^*}{\partial \mathbf{r}_{j'}} \phi_{\mathbf{r}_j(\mathbf{k}_j)} \right) - \frac{e_j \phi_{\mathbf{r}_j(\mathbf{k}_j)}^* A(\mathbf{r}_j) \phi_{\mathbf{r}_j(\mathbf{k}_j)}}{c} \right]}{\iiint d^3 \mathbf{r}_j / \phi_{\mathbf{r}_j(\mathbf{k}_j)}^2}, \quad (A4b)$$

where each single particle wave function has been normalized ($\iiint d^3 \mathbf{r}_j / \phi_{\mathbf{r}_j(\mathbf{k}_j)}^2 = 1$) to the region (of integration) that is used in the evaluation of the right-side (R.S.) of Eq. A4b.

These results, which are exact for the GS at $T=0$, in the bulk, are the many-body generalization (for charged particles in finite crystals) of the expression that relates the gradient of the eigenvalue $\varepsilon(\mathbf{k}_i)$ with respect to wave-vector \mathbf{k}_i to the local velocity (and current) in the bulk region. This relationship, in turn, is used in the semi-classical theory of conduction (which is traditionally derived, using a heuristic approach based on ‘‘independent quasi-particles’’, associated with the semi-classical theory, in the limit of bands that are derived using infinitely periodically ordered solids). Implicitly, the results apply for all charged particles (including protons), as in the conventional semi-classical theory. But with the exception of hydrogen and its isotopes, the average current from particular bands involving protons and core electrons is entirely negligible. Also, no net contribution to the current occurs when the summation over coordinates \mathbf{r}_i (on the L.S. of Eq. 22) and wave-vectors- \mathbf{k}_i (on the R.S) involves a filled band (which occurs when all values of \mathbf{k}_i in the First Brillouin Zone are included for a particular band). As in conventional band theory, filled bands do not contribute to the current because $\varepsilon(\mathbf{k}_i)$ is a periodic function, with respect to translations by a reciprocal lattice vector.

In the semi-classical theory, the single particle relationship, associated with Eq. 22 (in which the many-body wave function is constructed from exchange-symmetrized products of single particle wave functions), is used to derive particle fluxes, in which the perturbation $V - V'$ is finite, on the R.S. of Eq. 15. Then, (implicitly) surface effects are accounted for through the minimization procedure associated with Eqs. A1-A3. This means the remaining terms (omitted from Eq. 15) in Eqs. A4(a,b), associated with extending the many-body state into surface regions, vanish. In a $T=0$ state, in the absence of an external Electric Field (E), this can be justified using the asymptotic limit (alluded to above) in which both the charge and electrostatic field exponentially decay. In particular, provided the range over which any changes associated with this exponential decay can be appreciable is

considerably larger than the characteristic length of any unit cell, the effect of the decay can be treated using a slowly-varying (envelope) function that can be held constant during the integration over any particular integration in a unit cell outside the bulk region. Then, it follows that (since each integrand is periodic) the dependence of this envelope function on the flux or normalization, globally, in the numerator and denominator of Eqs. A4(a,b), appears as a portion of a common pre-factor of a single (but distinct) integral (associated with the flux or normalization) from a single unit cell. As a consequence, in their most general form, Eqs. A4(a,b) hold, but how they apply requires that a particular form of coupling in the surface region be approximately valid. In situations, where the bulk region remains neutral, and in regions near the bulk, when the change in charge, on the average, decreases in a smoothly varying fashion, that occurs over many unit cells, within any particular cell, as a consequence, $V-V'$ can effectively be viewed as not being effected by the presence of the surface. In this region of slowly-varying decay in charge and potential, from unit cell to unit cell, the net force that is applied at the boundaries of the solid can be averaged over many cells. Then, over the surface region, $V-V'$ can be approximated using a classical force, multiplied by the distance (associated with the surface region) where non-neutral forms of force apply. In this limit, the applied force merely shifts the zero of energy.

Thus, in this limit, to maintain charge neutrality, a net flux of charge can occur with respect to boundaries of the solid in which the imbalance in flux is associated with classically defined differences in E (associated with averaging the value of E over the entire solid) in regions (near surfaces and interfaces) where an imbalance in charge can occur. In particular, always, at low T , net flux of all charged particles to and from the bulk region vanishes. This can occur when equal amounts of charge enter and leave the bulk, in which the zero of momentum of the many-body state is allowed to shift, uniformly, and the only net force, acts on all of the particles uniformly. Then, effectively, a change in momentum at the boundary of the bulk leads to a perfectly rigid change in which all particles in the bulk move with a constant (fixed velocity) that is equivalent to a perfectly rigid form of interaction in which, effectively, all outside forces impart momentum directly to the center-of-mass of the solid. The associated shift is defined by the limit in which A and A' are different, non-uniform and non-periodic in the surface region but are required (on the average) to be uniformly constant in the bulk. This leads to a uniform (but time dependent) shift in the zero of momentum of the bulk, as defined by its instantaneous reference frame, relative to a particular time, and by its possible coupling (through the vector potential and static electromagnetic fields).

Since the bulk region is neutral, on the average, the value of its center of mass momentum $P_{cm,o} = p_o = M_{bulk} V_{cm,o}$, where p_o is the average zero of momentum (as defined earlier), M_{bulk} is the total mass of the bulk, and $V_{cm,o}$ is the absolute velocity of the bulk region. But since neither M_{bulk} or $V_{cm,o}$ can be measured (and neither quantity is conserved) without introducing external charge, it is only possible to relate $P_{cm,o}$ to the total center-of-mass momentum P_{cm} associated with both the bulk region ($P_{cm,o}$) and non-bulk region ($=P_{cm,nb}$) values of the momentum, using the relationship, $P_{cm} = P_{cm,o} + P_{cm,nb}$, and to changes in the velocity V_{cm} of the center-of-mass of the solid. In particular, in the absence of external electromagnetic fields (and external vector potentials), near the GS, provided the solid is neutral, on the average (with respect to individual unit cells), it follows that averaged over bulk and non-bulk regions, $P_{cm} = M V_{cm} = P_{cm,nb} + P_{cm,o} \equiv P_{cm,nb} + p_o$, where $M =$ total mass of the solid.

But at the boundaries of the bulk, a net accumulation of charge can occur, which means that although it is not possible to measure $M_{bulk} V_{cm,o}$ directly, it is possible to impose the requirement that, instantaneously, as a function of time (as $T \rightarrow 0$), no net acceleration of the bulk relative to non-bulk region be allowed to take place.

When this is true, $\frac{dM V_{cm}}{dt} = \frac{d(P_{cm,o} + P_{cm,nb})}{dt} = 0$, which means that $\frac{dp_o}{dt} = -\frac{dP_{cm,nb}}{dt} = \frac{dP_{cm,o}}{dt}$.

Since there is no charge, on the average, in the bulk, it also follows that the requirement that $\frac{dM V_{cm}}{dt} = 0$ instantaneously, as $T \rightarrow 0$, also applies both for the sum of forces that act independently either on (all) negatively or positively charged particles. Also, because positive and negative charges respond to external fields by accelerating in opposite directions, the requirement that zero net flux of particles (or energy) occur at the boundaries of the bulk region implies that in the GS, the net currents from bulk and non-bulk regions, associated with positive and negative charges, separately vanish. Then it is possible to define an instantaneous rate of change $\frac{dp_o}{dt}$ of the zero of

momentum, respectively, $\frac{dp_o}{dt} = \frac{dp_o^j}{dt}$, or $\frac{dp_o}{dt} = \frac{dp_o^j}{dt}$ for positively or negatively charged particles in the bulk region. For this reason, although it is not possible to determine, unambiguously, the value of the velocity of the center-of-mass $V_{cm,o}$ of the bulk region, it is possible to relate changes in the flux of each kind of (positively or

negatively charged) particle (and the associated currents) that result in response to changes in applied fields, based on the assumption that the bulk region remains in its ground state.

In particular, the resulting changes in flux occur through changes in M_{bulk} that result from the requirement that all changes in the bulk occur through rigid (Galilean) translations that only alter the many-body state of the GS by shifting the local zero of momentum of each coordinate (and total zero of momentum of the bulk). The changes in momentum (and mass) can be inferred, using Gauss's law (which is required to define the boundaries of the bulk region, and of the entire solid), and the following requirements: 1. For each rigid shift (through an effective Galilean transformation) of the bulk, separate values of $\Delta p_o = \Delta t \frac{d\mathbf{p}_o}{dt} = \Delta t \frac{d\mathbf{p}_o^{j'}}{dt}$ accompany the shift in momentum. (These values of Δp_o have opposite sign for situations associated with positively charged particles, which occur when $j''=j$, as opposed to situations associated with negatively charged particles, which occur when $j''=j'$.) 2. Each value of Δp_o ($\Delta p_o = \Delta p_o^j$ or $\Delta p_o = \Delta p_o^{j'}$, respectively for all positively or negatively charged particles) for each shift leads to a constant, uniform change of the vector potential in the bulk, and 3. The ground state, in bulk regions, is not altered by the sum of the two shifts, which means 4. The sum of external forces F , associated with changes resulting from the two shifts, vanishes at the boundaries of the bulk region. To determine $\Delta \mathbf{P}_{\text{cm},o}^j$ and $\Delta \mathbf{P}_{\text{cm},o}^{j'}$, it follows that in the

surface region $\mathbf{E} = -\frac{\partial \mathbf{A}}{c\partial t}$, and $\nabla \cdot \mathbf{A} = 0$. Then, in the presence of a constant, spatially uniform, externally applied E field, and constant, spatially uniform B field, or both, the difference between an externally applied vector potential $\mathbf{A}(\mathbf{x}, t)$ and the (time independent) ground state vector potential $\mathbf{A}_o(\mathbf{x})$ (that is used to define $\mathbf{P}_{\text{cm},nb}$) is defined by

$$\mathbf{A}(\mathbf{x}, t) - \mathbf{A}_o(\mathbf{x}) = (-\mathbf{E}ct + \frac{\mathbf{B} \times \mathbf{x}}{2}) . \quad (\text{A5})$$

The fourth requirement is satisfied when with respect to the ground state, externally applied forces in non-bulk regions are balanced in the same regions by existing forces. As a consequence, formally,

$$\begin{aligned} \frac{dM^j V_{\text{cm}}^j}{dt} &= \left(\frac{d \langle \Psi_{GS}^j | \mathbf{P}_{\text{cm},nb}^j - \mathbf{e}^j / c \mathbf{A}(\mathbf{x}^j) | \Psi_{GS}^j \rangle}{dt} \right) \\ &= \frac{\langle \Psi_{GS}^j | \frac{i[H_o, \mathbf{P}_{\text{cm},nb}^j]}{\hbar} + \frac{\mathbf{e}^j \mathbf{E}}{\hbar} + \mathbf{e}^j \frac{\mathbf{v}(\mathbf{x}_j)}{\hbar c} \times \mathbf{B} | \Psi_{GS}^j \rangle}{\langle \Psi_{GS} | \Psi_{GS} \rangle} \equiv 0 , \end{aligned} \quad (\text{A6a})$$

where $\mathbf{v}(\mathbf{x}_j)$ (=velocity of positively charged particles, as defined by Eq. 12), the only contributions to the integrations in the numerator occur from the non-bulk region (and its boundaries), H_o is the Hamiltonian, in the absence of outside perturbations, and the expectation value associated with the commutator, $\langle \Psi_{GS} | i[H_o, \mathbf{P}_{\text{cm},nb}^j] | \Psi_{GS} \rangle$, does not vanish because it involves an integration over a finite, limited volume (the non-bulk region). Also, here, and throughout, the notation Ψ_{GS}^j in the numerator of Eq. A6a, and the associated short-hand, notation $\mathbf{P}_{\text{cm},o}^j - \mathbf{e}_j \mathbf{A}(\mathbf{x}_j, t)$ in the first line, and subsequently (after substituting Eq. A5 and using the definition associated with time evolution) in the second line, refers to evaluating the portion of the expectation value of $\mathbf{P}_{\text{cm},nb} - e/c\mathbf{A}(\mathbf{x},t)$ in which the charge e_j and the vector potential \mathbf{A} and momentum $\mathbf{P}_{\text{cm},nb}$ are restricted to coordinates \mathbf{x}_j , that involve positively charged particles. In practice, this means that \mathbf{x}_j refers to a location where $\mathbf{e}_j = |e|$, and the dependence associated with changes in $\mathbf{P}_{\text{cm},nb}$ and changes in the electromagnetic fields, are included at locations where positively charged particles are allowed to couple to \mathbf{A} , through overlap between Ψ_{GS} and $\mathbf{e}_j \mathbf{A}(\mathbf{x}_j, t)$. Eq. A6(a), and remaining equations describing the zero of momentum, as written above and below, apply for positively charged particles. They also can be used to determine the zero of momentum that applies when the coordinates \mathbf{r}_j (associated with positively charged particles) are replaced with the comparable coordinates, \mathbf{r}_j' (associated with negatively charged particles) and each positive charge \mathbf{e}_j is replaced with a negative charge $\mathbf{e}_j' = -\mathbf{e}_j$.

Because relative changes in \mathbf{P}_{cm} alter the wave function globally (as in Eq.10), in establishing the zero of momentum (and velocity), changes involving the center-of-mass momentum in the non-bulk regions can be used to define comparable changes in the bulk region. Specifically, when $\frac{dMV_{cm}^j}{dt} = 0$ (as in Eq. A6a), for the center-of-mass (cm), it is possible to define a separate change in cm and force, associated with each positively or negatively charged particle (where $j=j$ for positively charged particles, and $j=j'$ for negatively charged particles). This means that $\frac{dP_{cm}^j}{dt} = \frac{dMV_{cm}^j}{dt} = \frac{dP_{cm,nb}^j}{dt} + \frac{dP_{cm,o}^j}{dt} = 0$, and $\frac{dP_{cm,nb}^j}{dt} = -\frac{dP_{cm,o}^j}{dt} = 0$. But then since the integration in the numerator extends only over the non-bulk region, it follows from Eq. A6a that

$$-\frac{\langle \Psi_{GS} | \mathbf{t} [H_o, \mathbf{P}_{cm}^j] | \Psi_{GS} \rangle_{non-bulk}}{\langle \Psi_{GS} | \Psi_{GS} \rangle} = -\frac{dP_{cm,nb}^j}{dt} = \frac{dP_{cm,o}^j}{dt} = +\frac{e^j \mathbf{E}}{\hbar} + e^j \frac{\mathbf{v}(\mathbf{x}_j)}{\hbar c} \times \mathbf{B}. \quad (\text{A6b})$$

Also, from Eq.A4a, it follows that for all particles, the average value of the total velocity $\mathbf{v}(\mathbf{x})$ (as in Eq. A6a) of a particular kind of particle can be expressed, using

$$\sum_j \mathbf{n}_{k_j} \nabla_{\mathbf{k}_j} \varepsilon(\mathbf{k}) = \sum_j \iiint d^3 r_j \mathbf{v}(\mathbf{x}_j). \quad (\text{A6c})$$

This relationship holds either for positively or negatively charged particles, and the sum over j involves all possible occupied and unoccupied band state eigenvalues (for each kind of particle): It also follows from the definition of $\mathbf{P}_{cm,o}^j$,

$$\frac{dP_{cm,o}^j}{dt} = \sum_{\{i\}} \frac{\hbar d\mathbf{k}_i^j}{dt}. \quad (\text{A6d})$$

But then when Eqs. A6d and A6c are substituted into Eq. A6b, separate summations involving \mathbf{k}^j occur on both sides of the resulting expression. In particular, for each value of $\frac{\hbar d\mathbf{k}_i^j}{dt}$ (from the summation on the R.S. of Eq. A6d) that appears on one-side of the resulting expression, a comparable term, of the form, $\nabla_{\mathbf{k}_j} \varepsilon(\mathbf{k}) = \iiint d^3 r_j \mathbf{v}(\mathbf{x}_j)$ (from the summation on the L.S. of Eq. A6c) appears on the opposite side of the

expression. Because all possible values of momentum (and overlap) are possible, each summation can involve a limited (but the same) number of terms. Thus, for the equation to be valid, for arbitrary forms of occupation, it follows that the dependence on the local zero of momentum (through \mathbf{k}) is systematically required to be balanced, term by term, on both sides of the equation. This means it is possible to assign a local, time-dependent change $\Delta \mathbf{k}_i = \frac{\Delta t d\mathbf{k}_i}{dt}$ for each component k_i of the wave-vector, independently, for positive or negative charges.

Then, using Eqs. A6a-d, it follows that for each value of the local zero of the wave-vector \mathbf{k} , for each particle,

$$\frac{d\mathbf{k}}{dt} = \mathbf{e}_{j^+} \mathbf{E} + \mathbf{e}_{j^-} \frac{\nabla_{\mathbf{k}} \varepsilon(\mathbf{k})}{c} \times \mathbf{B}. \quad (\text{A7})$$

As a consequence, a separate (positive or negative) shift $\Delta \mathbf{k}$ of the local wave-vector zero occurs for each (positively or negatively charged) particle. In each case, the magnitude of the shift is the same for each kind of particle for each value of \mathbf{k} . For the ground state in bulk regions, no net change in charge occurs. Because some charge can leave the solid and because (in the presence of magnetic fields) the effects associated with the gradients of the band state eigenvalues are different for ions than electrons, for each value of \mathbf{k} , $\Delta \mathbf{k}$ is very different for positively or negatively charged particles. Thus, both for ions and electrons relative to the surface (and to each other), effectively, the center-of-mass velocity (and momentum) of the Bulk can (and does) change. As a function of time, this is equivalent to allowing all of the various wave-vectors to be shifted by $\frac{\pm \Delta \mathbf{p}(t)}{\hbar}$, based on Eq. A7, in bulk regions. (The positive charge in the prefactor of \mathbf{E} is used for positive charges, and the negative sign is used otherwise.) Then, when charge is free to flow into and away from the bulk region, a quasi-steady state can evolve,

that can be described, based on the interpretation that each "particle" moves (in the sense that its average current is described by Eqs. A4(a,b)), while its wave-vector changes in time, from $\mathbf{k}=\mathbf{k}_0$ to $\mathbf{k} = \mathbf{k}_0 \pm e \frac{(\mathbf{E} + \nabla_{\mathbf{k}} \epsilon / c \times \mathbf{B})t}{\hbar}$.

The associated picture is a generalization of the semi-classical equations of motion (that are used in the associated theory of conductivity and transport). A requirement for its success is that the bulk region remain neutral and a quasi-equilibrium be established, in which charge in non-bulk regions redistributes itself sufficiently rapidly that the value of t not become so large that the value of k is forced to be comparable to a reciprocal lattice vector G_1 . If this occurs, in fact, the zero of momentum of the bulk becomes sufficiently large that each wave-vector is shifted by the same finite, amount, G_1/N . In the associated effect, which is the basis of Umklapp (or U-) processes, all charged particles of a particular kind instantly acquire the same, small (but finite) amount of momentum, and the bulk region, as a whole, recoils, relative to the surface.

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