Semiconductors and Insulators

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(Dated: December 13, 2024)

I. ELECTRONS IN SOLIDS: INSULATORS AND METALS

A. Electronic Hamiltonian

Let us consider the problem of describing simple materials and consider the following Hamiltonian as a starting point

$$H_N = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i,j}\frac{Z_j e^2}{|\mathbf{r}_i-\mathbf{R}_j|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} \tag{1}$$

where $\mathbf{r}_i$ are the electronic positions, m and e are the elecron mass and charge, respectively, and Z_j is the charge of the ion at position $\mathbf{R}_j$. The Hamiltonian neglects the nuclear (zero-point) motion (phonons), and subsequent electron-phonon coupling effects. From a pure energetic point of view, this is in general well justified, as both effects are suppressed by some power of $(m/M_j)^{1/4}$, where M_j are the nuclear mass. The Hamiltonian (1) can be considered as the starting point for the calculation of nuclear quantum effects and electron-phonon coupling.

B. Crystals

In the following, we will assume a solid with perfect crytalline order, so that the crystalline potential

$$U(\mathbf{r}) = -\sum_j \frac{Z_j e^2}{|\mathbf{r}-\mathbf{R}_j|} \tag{2}$$

is invariant with respect to discrete translations $\mathbf{t}_\alpha$, $U(\mathbf{r}+\mathbf{t}_\alpha)=U(\mathbf{r})$ where $\mathbf{t}_\alpha$, $\alpha=1,2,3$ are some basis vectors which span the fundamental translations of the crystal. This will also imply the invariance of the total N electron density of any energy eigenfunction

$$H\Psi_n(\mathbf{r}_1,\dots,\mathbf{r}_N) = E_n\Psi_n(\mathbf{r}_1,\dots\mathbf{r}_N) \tag{3}$$

$$|\Psi_n(\mathbf{r}_1+\mathbf{t}_\alpha,\mathbf{r}_2+\mathbf{t}_\alpha,\dots,\mathbf{r}_N+\mathbf{t}_\alpha)| = |\Psi_n(\mathbf{r}_1,\dots,\mathbf{r}_N)| \tag{4}$$

Using periodic boundary conditions of our system, $\Psi(\dots,\mathbf{r}_i+L,\dots)=\Psi(\dots,\mathbf{r}_i,\dots)$, we can classify all eigenfunctions by the phase aquired by a global translation by a crystal vector

$$\Psi_{n\mathbf{k}}(\mathbf{r}_1+\mathbf{t}_\alpha,\mathbf{r}_2+\mathbf{t}_\alpha,\dots,\mathbf{r}_N+\mathbf{t}_\alpha) = e^{i\mathbf{k}\cdot\mathbf{t}_\alpha}\Psi_{n\mathbf{k}}(\mathbf{r}_1,\dots,\mathbf{r}_N) \tag{5}$$

where $\mathbf{k}$ becomes a dense (continuous) label in the limit of an infinite system $L\to\infty$, and can be chosen to be within the first Brillouin zone. For each value of $\mathbf{k}$, we will have an infinite number of excitations, $E^N_{n\mathbf{k}}$, labelled by the discrete index, n. We may assume that the ground state $n=0$, will have $\mathbf{k}=0$.

When probing/ calculating properties within linear response, we may expect simplifications when we can assume that all excitations will be gapped, e.g. $E_{n0}-E_{00}\geq\Delta>0$ for $n\neq 0$. Please note that excitations changing the cyrstal momentum $\mathbf{k}$ are expected to be continuously connected (no gap).

C. Single electron excitations

Let us consider to add an electron to our system in the ground state. Sounds simple for theoreticians, however, we may have some practical problems. Since total charge is conserved, we will encouter a charged cyrstal which will interact via Coulomb interactions with the world outside the material which we don't want to include in our

theoretical desription. A different situation will be if we consider that the additional electron charge is compensated by increasing the charge of one ion by one. However, this will break our translational symmetry so that we cannot make use anymore of symmetry considerations to simplify some aspects of our problem.

The solution for theoreticians is to consider the situation where the additional electronic charge is compensated by a smeared out, homogeneous background charge. Alternatively, one may consider an increase of all nuclear charges by $1/N$. Both cases do not affect our crystal symmetry. We will use the homogeneous background charge, which is most commonly used. Effects of a positive charge inhomogenity, e.g. due to doping, modelling more concrete experimental probes, can be considered (perturbatively) in a second step.

It is then clear that we can again classify our $N+1$ energy eigenstates, $E_{n\mathbf{k}}^{N+1}$, by crystal momenta $\mathbf{k}$, and a discrete band index n. Then we may define our perfect (band) insulator by the situation where all excitations of our $N+1$ electron state are gapped with respect to the N particle ground state

$$E_{n0}^{N+1} - E_{00}^{N+1} \geq \Delta > 0 \tag{6}$$

When the gap vanishes, we may expect qualitative changes in physical properties, more typical for metals.

We assumed that the $N+1$ ground state has $\mathbf{k} = 0$. With respect to excitations changing crystal momenta, we then expect a regular behavior

$$E_{n\mathbf{k}}^{N+1} = E_{00}N + 1 + \frac{1}{2}\sum_{\alpha\beta}\mu_{\alpha\beta}^{-1}k_\alpha k_\beta \tag{7}$$

where μ is the effective mass tensor.

Of course, all these considerations can be directly extended to the hole sector having $N-1$ electrons.

D. From many-electron wave functions to single particle band theory

Kohn [1, 2] has outlined how single particle band theory emerges from the solution of the many-electron Schrödinger equation. He considered an impurity problem with a perturbation via an external charge q at the origin of the $N+1$ electron system

$$v(r) = -q\frac{e^2}{\sum_i |\mathbf{r}_i|} + q\sum_j \frac{Z_j e^2}{|\mathbf{R}_j|} \tag{8}$$

and we loo for the new ground state

$$(H+v)\Psi = E\Psi \tag{9}$$

Our external potential breaks the discrete translational symmetry of the crystal. We write down and expansion of the new energy eigenfunction in terms of the unpertubed ones

$$\Psi = \sum_{n\mathbf{k}} a_{n\mathbf{k}}\Psi_{n\mathbf{k}}^{N+1} \tag{10}$$

By definition, our insulator states with $n > 0$ are gapped with respect to the $N+1$ ground state $n = 0$, so that we can use quasi-degererate perturbation theory considering only states $\Psi_{0\mathbf{k}}$

$$(E_{0\mathbf{k}} - E)a_{0\mathbf{k}} + \sum_{\mathbf{k}'}\langle\Psi_{0\mathbf{k}}|v|\Psi_{0\mathbf{k}'}\rangle a_{0\mathbf{k}'} = 0 \tag{11}$$

where the summation over $\mathbf{k}'$ extends over all wave vectors in the first Brillouin zone.

In Fourier space, our perturbation writes

$$v(r) = const - q\frac{1}{V}\sum_{\mathbf{k}}\frac{e^2}{4\pi k^2}\rho_{\mathbf{k}} \tag{12}$$

where $\rho_{\mathbf{k}} = \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i}$ is the density operator in Fourier space. Since $\rho_{\mathbf{k}}$ can only couple $\Psi_{\mathbf{q}}$ with $\Psi_{\mathbf{q}+\mathbf{k}}$ (use behavior under lattice translations) we have

$$(E_{0\mathbf{k}} - E')a_{0\mathbf{k}} - \frac{q}{V}\sum_{\mathbf{k}'\neq\mathbf{k}}\frac{e^2}{4\pi(\mathbf{k}'-\mathbf{k})^2}\langle\Psi_{0\mathbf{k}}|\rho_{\mathbf{k}-\mathbf{k}'}|\Psi_{0\mathbf{k}'}\rangle a_{0\mathbf{k}'} = 0 \tag{13}$$

where E' contains the constant shift from the $\mathbf{k} = \mathbf{k}'$ term.

Kohn first argued [1] and then showed within perturbation theory [2] that

$$\lim_{\mathbf{q}\to 0} \langle \Psi_{0\mathbf{k}+\mathbf{q}} | \rho_{\mathbf{q}} | \Psi_{\mathbf{k}} \rangle = \frac{1}{\epsilon} \quad \mathbf{q} \neq 0 \tag{14}$$

where ϵ is the dielectric constant for $\mathbf{k} \to 0$.

Inserting this limiting value into our effective Schrödinger equation above, we get

$$(E_{0\mathbf{k}} - E')a_{0\mathbf{k}} - \frac{q}{V} \sum_{\mathbf{k}' \neq \mathbf{k}} \frac{e^2}{4\pi\epsilon(\mathbf{k}' - \mathbf{k})^2} a_{0\mathbf{k}'} = 0 \tag{15}$$

Using the effective mass approximation for $E_{0\mathbf{k}}$, we recover an effecive Schrödinger equation of a particle of effective mass μ interacting with Coulomb potential of charge q in a material of dielectric constant ϵ. Of course, the relation Eq. (14) only holds for wave vectors with small k, as well as due to the restriction of the summation within the Brillouin zone, the $1/r$ behavior is only obtained at distances large compared to lattice sites.

We could now forget about the $N+1$ electron wave functions, we have expanded in, and would recover just a single electron band theory equation.

II. DIAGRAMMATIC CONSIDERATIONS

In order to proof Eq. (14), we have to first define what we mean by dielectric constant. A standard definition of the dielectric constant is via linear response of the undoped material with N electrons with respect to an external perturbation, v,

$$u = u_q \left(\rho_{\mathbf{q}} + \rho_{-\mathbf{q}} \right) \tag{16}$$

The perturbed energy $E_u = E_{00}^N + \chi_q u_q^2 + \dots$ defines the static density-density response function χ_q which then gives the dielectric constant via $(1/\epsilon - 1) = v_q \chi_q$ where $v_q = 4\pi/q^2$ is the Fourier transform of the Coulomb potential.

A. Diagrams...

With respect to our previous diagrammatic expansions, we now have to start from a non-interacting system which includes the periodic crysal potential. Using the discrete lattice symmetry, our non-interacting Green's function will be diagonal in the crystal momentum $\mathbf{k}$ and in the discrete band index n, e.g. $G_0^{-1}(\mathbf{k}, n; z) = z + \mu - \varepsilon_{n\mathbf{k}}$. The chemical potential is chosen such that we are in an insulating state, e.g. $\varepsilon_{0\mathbf{k}} - \mu < 0 < \varepsilon_{n\mathbf{k}} - \mu$, for $n \neq 0$ and all $\mathbf{k}$ (we have assumed just one fully occupied band, $n = 0$).

Coulomb interactions will then introduce changes in $\mathbf{k}$ and n but the total crystal momentum will still be conserved at each interaction vertex. It is then rather straighforward to adapt our diagramatic rules.

We can then also introduce vertices with respect to the external potential u. At one of these vertices, the crystal momentum is changed by $\mathbf{q}$ and inter band transitions may occur. To obtain the linear response, we only need to consider graphs containing two u vertices.

We then may isolate potential divergent terms of the Coulomb interaction as previously. The leading suspect are bubble diagrams, which now have to be extended with a summation over the discrete band index.

$$B_0(k, n; z = 0) \;=\; \sum_m \int \frac{d\mathbf{p}}{(2\pi)^3} \frac{f_F(\varepsilon_{m\mathbf{p}} - \mu) - f_F(\varepsilon_{n\mathbf{k}+\mathbf{p}} - \mu)}{\varepsilon_{m\mathbf{p}} - \varepsilon_{n\mathbf{p}+\mathbf{k}}} \tag{17}$$

Setting $n = 0$, we see that only terms with $m > 0$ contribute. However due to the insulating behavior, the denominator is never vanishing. Therefore we will get a regular expansion around $k = 0$ which has to start with k^2. We then see that diagrams involving $v_q B_0(q)$ will remain always finite in the limit of $q \to 0$. Divergencies due to the Coulomb potential will not play any major role in the perturbation expansion.

The diagrammatic expansion for χ_q will be very similar to diagrams involving our Coulomb potential v_q with open ends of the vertex (and replacing the factor $4\pi/q^2$ by u_q). We can see that basically all diagrams considered for $v_{eff}(q)$ can be adapted for the ones involving χ by simply replacing the v_q of one end by u_q.

B. Diagrams for the $N+1$ system

are the same as the N particle system, however, now the chemical potential will be such that we have to include one state of the excited band in the sum. We might now write down diagrams for Eq. (14) and identify the leading order terms for $q \to 0$ with the one making up the ground state dielectric constant following [2]. Equivalently we could consider the density density response of the $N+1$ particle system. From the spectral decomposition, the changes with respect to the density-density reponse of the N-particle system will go like

$$\frac{|\langle \Psi^{N+1}_{1\mathbf{q}} | \rho_{\mathbf{q}} | \Psi^{N+1}_{10} \rangle|^2}{E^{N+1}_{1\mathbf{k}} - E^{N+1}_{10}} \sim \mu q^{-2}/2\epsilon^2 \tag{18}$$

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[1] W. Kohn, Phys. Rev. **105**, 509 (1957).
[2] W. Kohn, Phys. Rev. **110**, 857 (1958).