

Born Oppenheimer Approximation

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1 Biographical Background

The article, *Zur Quantentheorie der Molekeln (On the Quantum Theory of Molecules)* [4], discussed in this review was initially published in 1927 by Max Born and his student at the time Robert Oppenheimer. Born worked at University of Gottingen in Germany and was an important figure in the development of Quantum Mechanics. Along with Heisenberg, Born developed the matrix representation of quantum mechanics and won the noble prize in 1954 for pointing out the now ubiquitous interpretation of $\Psi^*\Psi$ as the probability density. In addition to his role in the development of quantum mechanics, Born also made many important contributions to our understanding of nuclear physics, atomic and molecular physics, and the physics of solids. Robert Oppenheimer became a faculty member in the department of physics at UC Berkeley. He is arguable most known for his role in the Manhattan project and subsequently for being very outspoken on the topic of nuclear non-proliferation. In addition to his early work on Quantum mechanics and nuclear physics, Oppenheimer

also made important contributions to Quantum Field Theory, and astrophysics including key papers on neutron stars, black holes, and cosmic rays.

2 Definition of Problem

In *Zur Quantentheorie der Molekeln* [4], Born and Oppenheimer set out to find a general method to solve for the energy levels and wave functions describing the quantum dynamics of electrons and ions in a molecule. The case that Born and Oppenheimer make here is that because of the large separation in mass of the electrons, m , and ions (protons and neutrons), M , there will be a large separation in velocity of the two objects which can be exploited to simplify the problem of computing molecular energies.

When we take the approximation that the ionic motion is much slower than the electronic motion we can treat the ionic motion as an adiabatic perturbation on the electron system which will not shift the electronic states. The Hamiltonian can be broken into terms in orders of the small perturbation parameter $\kappa = \left(\frac{m}{M}\right)^{1/4}$. It is shown in the article that only even powers of κ contribute to the energy of the system. The dominant term of order κ^0 is the electronic energy, the quadratic term describes the ionic vibrations, and the quartic term describes the ionic rotational energy, higher order vibrational energy and couplings between the rotations and ionic and electronic states.

Because of this adiabatic approximation and this perturbative expansion order naturally separating the electronic and ionic terms we can iteratively solve the problem in progressively higher orders. The electronic wave functions and energies will only depend on the mean ionic coordinates through the potential created by the ions and equivalently the ionic wave functions will only be functions of the ionic coordinates. Since the electronic Hamiltonian has a potential term that is a function of the ionic *mean* positions the electronic energies will be functions of the ionic coordinates. The effect of this is that when one goes to calculate the quadratic term in the expansion for the ionic motion the eigenvalues of the zeroth order term from the electrons serve as an effective potential for the ions. As is typical with perturbation theory, as one goes to higher orders you continue to feed these lower order solutions into the Hamiltonian and wave functions of the next higher order. It is shown that in order to get the full zeroth order wave function for a general molecular system you must continue with the perturbation up to the fourth order in the Hamiltonian.

3 Initial Formulation

Here we step through the formulation of the approximation given by Born and Oppenheimer in the original 1927 paper.

3.1 Definition of Coordinates and General Terms

The coordinates (and mass) for the electrons in the molecule are given by lower case letters m , x_k , y_k , z_k and by capital letters for the nuclei, M_l , X_l , Y_l , Z_l . The parameter which will be shown to be the perturbation parameter is given by:

$$\kappa = \left(\frac{m}{M} \right)^{1/4} \quad (1)$$

Where M is the average value of M_l . Since the electron and ion masses are separated by $\sim 10^3$ this is indeed a small number good for perturbation. The potential, U , is left as a general function of x , and X , and to form the Hamiltonian we also need the kinetic terms. We take the kinetic energy for the electron as

$$T_E = -\frac{\hbar^2}{2m} \sum_x \sum_k \frac{\partial^2}{\partial x_k^2} \quad (2)$$

and for the nuclei as

$$T_N = -\kappa^4 \frac{\hbar^2}{2m} \sum_X \sum_l \mu_l \frac{\partial^2}{\partial X_l^2} \quad (3)$$

where $\mu_l = M/M_l$ is a factor of order unity. Given the potential and two kinetic terms the total energy for the system is given by

$$H = H_0 + \kappa^4 H_1 \quad (4)$$

Where $H_0(x, \frac{\partial}{\partial x}; X) = T_E + U$ is the unperturbed Hamiltonian describing the electronic system assuming fixed nuclei and $\kappa^4 H_1(\frac{\partial}{\partial X}) = T_N$ is the perturbation due to the motion of the nuclei. The coordinates, X , for the nuclei can then be transformed to further separate the Hamiltonian. We can take $3N - 6$ functions that define the relative positions of the nuclei, $\xi_i(X)$ and 6 additional functions that define the position (translation) and orientation (rotation) of the total configuration in space, $\theta_i(X)$. One can translate between the rectilinear coordinates, X_l and these new coordinates by appropriate translations and rotations. This transformation now allows us to rewrite the nuclear part of the Hamiltonian as:

$$H_1 = H_{\xi\xi} + H_{\xi\theta} + H_{\theta\theta} \quad (5)$$

where the subscript denotes that the function is linear homogenous in the partial derivatives of the subscripts (i.e. $H_{\xi\xi}$ contains terms $\frac{\partial^2}{\partial \xi_i \partial \xi_j}$). An important point here is that the coefficient of $\frac{\partial^2}{\partial \xi_i \partial \xi_j}$ is independent of the position in space (θ_i) while there will be spatial dependence in the coefficients of $\frac{\partial}{\partial \xi_i}$ in $H_{\xi\theta}$ and in the coefficients of $\frac{\partial^2}{\partial \theta_i \partial \theta_j}$ in $H_{\theta\theta}$. This fact is exploited in the perturbation expansion in later steps. This is all we need to set up the Schrodinger Equation eigenvalue problem:

$$(H_0 + \kappa^4 H_1 - W)\psi = 0 \quad (6)$$

3.2 Electronic Motion for Stationary Nuclei: the Potential Energy Surface

The unperturbed Hamiltonian ($\kappa = 0$) gives a differential equation only in the electron coordinates, x_k , and the **eigenvalues of this system are only functions of the mean nuclear coordinates, X_l** . The eigenvalue problem for this system becomes:

$$\left\{ H_0 \left(x, \frac{\partial}{\partial x}; \xi, \theta \right) - V_n(\xi) \right\} \phi_n(x; \xi, \theta) = 0 \quad (7)$$

The eigenvalues, $V_n(\xi)$ define a potential energy surface for the nuclear motion. For the perturbation expansion we need to show the relation between derivatives of the Hamiltonian and derivatives of this potential. To do this we can take $\xi_i \rightarrow \xi_i + \kappa \zeta_i$ so that we can differentiate with respect to κ . **This makes explicit the small deviations, ζ , of the nuclei from their mean positions, ξ** . Now we can expand in κ

$$V_n(\xi + \kappa \zeta) = V_n^{(0)} + \kappa V_n^{(1)} + \kappa^2 V_n^{(2)} + \dots \quad (8)$$

The superscript denotes the order of partial derivatives so $V_n^{(1)}$ will be linear in ζ and have a first derivative of $V_n^{(0)}$ while $V_n^{(2)}$ will be quadratic in ζ and have a second derivative of $V_n^{(0)}$ as:

$$V_n^{(2)} = \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \xi_i \partial \xi_j} \quad (9)$$

The Hamiltonian and wave functions can also be expanded in the same way such that we arrive at:

$$H_0 = H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2 H_0^{(2)} + \dots \quad (10)$$

$$\phi_n = \phi_n^{(0)} + \kappa \phi_n^{(1)} + \kappa^2 \phi_n^{(2)} + \dots \quad (11)$$

The higher order wave functions can be recast into expansions of the unperturbed Hamiltonian wave functions by:

$$\phi_n^{(r)} = \sum_{n'} u_{nn'}^{(r)} \phi_{n'}^{(0)} \quad (12)$$

Where $u_{nn'}^{(r)}$ is a polynomial of that contains ζ_i to the r th power $u_{nn'}^{(2)}$ for instance is given by:

$$u_{nn'}^{(2)} = \sum_{ij} \zeta_i \zeta_j \int \phi_{n'}^{(0)*} \frac{\partial^2 \phi_n^{(0)}}{\partial \xi_i \partial \xi_j} \quad (13)$$

Any derivatives on operators, F , can be recast in the same way following:

$$F_{nn'}^{(r)} = \sum_{n''} u_{nn''}^{(r)} F_{n''n'} \quad (14)$$

With this laid out we can substitute eq. 8 and eq. 10 into eq. 7 then multiply by $\phi_{n'}^{(0)*}$, and integrate over x to enforce orthogonality. Then by exploiting eq. 14 we arrive at the following relations:

$$u_{nn'}^{(1)}(V_{n'}^{(0)} - V_n^{(0)}) + (H_0^{(1)})_{nn'} - V_n^{(1)}\delta_{nn'} = 0 \quad (15a)$$

$$u_{nn'}^{(2)}(V_{n'}^{(0)} - V_n^{(0)}) + (H_0^{(1)} - V_n^{(1)})_{nn'} + (H_0^{(2)})_{nn'} - V_n^{(2)}\delta_{nn'} = 0 \quad (15b)$$

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This gives the prescription for calculating successively higher order terms in the perturbation in terms of the lower order terms which we can employ to set up the approximation for molecular problem explicitly.

Since $\frac{\partial}{\partial \xi} = \frac{1}{\kappa} \frac{\partial}{\partial \zeta}$ we can expand the nuclear Hamiltonian from eq. 4 as:

$$\begin{aligned} \kappa^4 H_1(X, \frac{\partial}{\partial X}) &= \kappa^4 \left(\frac{1}{\kappa^2} H_{\zeta\zeta} + \frac{1}{\kappa} H_{\zeta\theta} + H_{\theta\theta} \right) \\ &= \kappa^2 H_{\zeta\zeta}^{(0)} + \kappa^3 \left(H_{\zeta\theta}^{(0)} + H_{\zeta\zeta}^{(1)} \right) + \kappa^4 \left(H_{\theta\theta}^{(0)} + H_{\zeta\theta}^{(1)} + H_{\zeta\zeta}^{(2)} \right) + \dots \end{aligned} \quad (16)$$

Combining eq. 10 and eq. 16 the total energy operator is:

$$\begin{aligned} H &= H_0 + \kappa H_0^{(1)} + \kappa^2 (H_0^{(2)} + H_{\zeta\zeta}^{(0)}) + \kappa^3 \left(H_0^{(3)} + H_{\zeta\theta}^{(0)} + H_{\zeta\zeta}^{(1)} \right) \\ &\quad + \kappa^4 \left(H_0^{(4)} + H_{\theta\theta}^{(0)} + H_{\zeta\theta}^{(1)} + H_{\zeta\zeta}^{(2)} \right) + \dots \end{aligned} \quad (17)$$

The total system energy, W , and eigenfunction, ψ can be expanded in the same way. Through the expansion we will show that in order to get all of the quantum numbers and the zeroeth order eigenfunction we need equations up to the fourth order for the energy. These equations are:

$$(H_0^{(0)} - W^{(0)})\psi^{(0)} = 0 \quad (18a)$$

$$(H_0^{(0)} - W^{(0)})\psi^{(1)} = (W^{(1)} - H_0^{(1)})\psi^{(0)} \quad (18b)$$

$$(H_0^{(0)} - W^{(0)})\psi^{(2)} = (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^{(0)})\psi^{(0)} + (W^{(1)} - H_0^{(1)})\psi^{(1)} \quad (18c)$$

$$\begin{aligned} (H_0^{(0)} - W^{(0)})\psi^{(3)} &= (W^{(3)} - H_0^{(3)} - H_{\zeta\zeta}^{(1)} - H_{\zeta\theta}^{(0)})\psi^{(0)} \\ &\quad + (W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^{(0)})\psi^{(1)} + (W^{(1)} - H_0^{(1)})\psi^{(2)} \end{aligned} \quad (18d)$$

$$\begin{aligned} (H_0^{(0)} - W^{(0)})\psi^{(4)} &= (W^{(4)} - H_0^{(4)} - H_{\theta\theta}^{(0)} - H_{\zeta\theta}^{(1)} - H_{\zeta\zeta}^{(2)})\psi^{(0)} \\ &\quad + (W^{(3)} - H_0^{(3)} - H_{\zeta\theta}^{(0)} - H_{\zeta\zeta}^{(1)})\psi^{(1)} \end{aligned} \quad (18e)$$

$$+ (W^{(2)} - H_0^{(2)} - H_{\zeta\theta}^{(0)})\psi^{(2)} + (W^{(1)} - H_0^{(1)})\psi^{(3)}$$

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3.3 Zeroth to Fourth Order Approximate Solutions

In [section 3.2](#) we found that for fixed nuclei the electronic eigenvalues and eigenvectors are $V_n^{(0)}$ and $\phi_n^{(0)}$ respectively. We can then write the general solution for the zeroeth order wave function as

$$\psi_n^{(0)} = \chi_n^{(0)}(\zeta, \theta) \phi_n^{(0)}(x; \xi, \theta) \quad (19)$$

Where $\chi_n^{(0)}(\zeta, \theta)$ is a function of the nuclear coordinates which will be determined from the higher order equations. We can now move to the first order equation ([eq. 18b](#)) and point out that it is only solvable when the RHS is orthogonal to $\psi_n^{(0)}$ which leads to the condition

$$\left\{ \left(H_0^{(1)} \right)_{nn} - W^{(1)} \right\} \chi_n^{(0)}(\zeta, \theta) = 0 \quad (20)$$

The curly brackets must be a constant so $W^{(1)} = \left(H_0^{(1)} \right)_{nn} = 0$ from this and [eq. 15a](#) and [eq. 10](#) we find that

$$\frac{\partial V_m}{\partial \xi_i} = 0 \quad (21)$$

This puts another constraint on this method, namely **the coordinates ξ_i must be chosen to be at extrema of of the electronic energy surface**. The first order equation ([eq. 18b](#)) then reduces to

$$\left(H_0^{(0)} - V_n^{(0)} \right) \psi^{(1)} = -H_0^{(1)} \chi_n^{(0)} \phi_n^{(0)} \quad (22)$$

The general solution to this is

$$\psi_n^{(1)} = \chi_n^{(0)} \phi_n^{(1)} + \chi_n^{(1)} \phi_n^{(0)} \quad (23)$$

Where $\chi_n^{(1)}$ is a new function of ξ and θ that needs to be determined from the higher order equations. So we now move on to the second order equation ([eq. 18c](#)) which after substituting the lower order solutions is:

$$\begin{aligned} \left(H_0^{(0)} - W^{(0)} \right) \psi^{(2)} &= \left(W^{(2)} - H_0^{(2)} - H_{\zeta\zeta}^{(0)} \right) \chi_n^{(0)} \phi_n^{(0)} \\ &\quad - H_0^{(1)} \left(\chi_n^{(0)} \phi_n^{(1)} + \chi_n^{(1)} \phi_n^{(0)} \right) \end{aligned} \quad (24)$$

From [eq. 15b](#) and the condition from the first order approximation that $V_n^{(1)} = 0$ we get that

$$\left(H_0^{(2)} \right)_{nn} + \left(H_0^{(1)} \right)_{nn}^{(1)} = V_n^{(2)} \quad (25)$$

So including this and again insisting that the RHS of [eq. 18c](#) is orthogonal to $\phi_n^{(0)}$ we arrive at the condition

$$\left\{ H_{\zeta\zeta}^{(0)} \left(\xi, \frac{\partial^2}{\partial \zeta_i \partial \zeta_j} \right) + \frac{1}{2} \sum_{ij} \zeta_i \zeta_j \frac{\partial^2 V_n}{\partial \zeta_i \partial \zeta_j} - W_n^{(2)} \right\} \chi_n^{(0)} = 0 \quad (26)$$

This is the equation for harmonic motion of the nuclei. Here we note two important points, **1) it is clear here that the second derivative of the electronic eigenvalues $V_n(\xi)$ play the role of a potential function for the nuclei and 2) for this to be a stable oscillation the condition from eq. 21 must be strengthened to insist that the ξ_i are chosen to be on minima not just extrema of V_n .**

Eq. 26 is separable by transforming ζ_i to normal coordinates of the oscillations, η_i . The eigenvalues of this system defined by Eq. 26 are $\sigma_{ns}^{(0)}(\zeta)$ where the index s is a new quantum number indexing the vibrational modes. The general solution is then

$$W^{(2)} = W_{ns}^{(2)} \quad (27a)$$

$$\chi_n^{(0)} = \chi_{ns}^{(0)} = \rho_{ns}^{(0)}(\theta)\sigma_{ns}^{(0)}(\zeta) \quad (27b)$$

Where $\rho_{ns}^{(0)}(\theta)$ is a new function only of the coordinate θ that defines the orientation of the arrangement of nuclei which is left to be determined from the higher order approximations.

It should be noted here that from the PDE eq. 26 it is known that $\sigma_{ns}^{(0)}(\zeta)$ consists of orthogonal Hermite functions for the normal coordinates. These functions oscillate in the classically allowed region and go to zero exponentially outside of the classically allowed region. This corroborates the assertion from 3.2 that the nuclear displacement is small, $\mathcal{O}(\kappa)$, about the mean nuclear positions.

With this new quantum number, s , we can now construct operators on ζ in the orthogonal basis including the vibrational quantum number of the form

$$\Phi_{nn'} = \int \sigma_{n's'}^{(0)*} \Phi \sigma_{ns}^{(0)} d\zeta \quad (28)$$

Like the procedure followed for the lower orders we can substitute eq. 26 in eq. 24 which will lead us to the general solution for the second order wave function:

$$\psi_n^{(2)} = \chi_{ns}^{(0)} \phi_n^{(2)} + \chi_{ns}^{(1)} \phi_n^{(1)} + \chi_{ns}^{(2)} \phi_n^{(0)} \quad (29)$$

Here again we have a new function $\chi_{ns}^{(2)}(\zeta_i, \theta_i)$ which is determined from the higher order equations. We now proceed in the same way to the third and higher order approximate solution these get notationally and practically more cumbersome to solve and they are spelled out explicitly in the original text. Here I will just state the resultant eigenvalues and wave functions for these higher terms and discuss their implications. The third order equation yields a differential equation for $\rho_{ns}^{(0)}$

$$\left(F_{nn}^{(3,3)} - W^{(3)} \right) \rho_{ns}^{(0)} = 0 \quad (30)$$

With the $F_{nn'}^{(3)}$ is given by

$$F_{nn'} = F_{nn'}^{(3,1)} \chi_{ns}^{(2)} + F_{nn'}^{(3,2)} \chi_{ns}^{(1)} + F_{nn'}^{(3,3)} \chi_{ns}^{(0)} \quad (31)$$

With the terms of F given by matching terms in eq. 18d. Because $F_{nn}^{(3,3)}$ is a polynomial of odd order all terms in the ζ matrix vanishes meaning that **there is no contribution from the third order equation to the total energy** ($W^{(3)} = 0$) and $\rho_{ns}^{(0)}$ **remains undetermined**. The general solution for the third order wave function then becomes:

$$\psi_n^{(3)} = \sum_{n'}' \left(G_{nn'}^{(3,1)} \chi_{ns}^{(2)} \phi_{n'}^{(0)} + G_{nn'}^{(3,2)} \chi_{ns}^{(1)} \phi_{n'}^{(0)} + G_{nn'}^{(3,3)} \chi_{ns}^{(0)} \phi_{n'}^{(0)} \right) \quad (32)$$

Where G is the common matrix element of higher order perturbation theory which contains a division by the difference in the energy states that the operator is connecting:

$$G_{nn'}^{(3,i)} = \frac{F_{nn'}^{(3,i)}}{V_n^{(0)} - V_{n'}^{(0)}} \quad (33)$$

The fourth order equation finally yields an equation for $\rho_{ns}^{(0)}$ namely:

$$\left(F_{nn}^{(4,4)} + \left(F_{nn}^{(4,3)} \right)_{ss}^{(1)} - W^{(3)} \right) \rho_{ns}^{(0)} = 0 \quad (34)$$

Where the functions $F_{nn}^{(4,i)}$ are defined the same as $F_{nn}^{(3,i)}$ but by matching terms in eq. 18e instead of eq. 18d. This equation contains terms that correspond to asymmetric top-like rotational modes including terms that couple the top motion and the electronic motion, terms that couple the top motion and angular momentum associated with the nuclear vibrations and terms that correspond to additional vibrational modes with energy $\mathcal{O}(\kappa^4)$. Separating out the vibrational part, eq. 34 yields

$$W^{(4)} = W_{n sr}^{(4)} \quad (35a)$$

$$\rho_{ns}^{(0)} = \rho_{n sr}^{(0)}(0) \quad (35b)$$

Where r is the final quantum number we need to describe the system corresponding to the indices of the rotational modes. The higher order equations yield couplings between the different modes but do not introduce any new quantum numbers. We now have enough information to construct the zeroeth order wave function

$$\psi_{n sr}(x, \zeta, \theta) = \phi_n^{(0)}(x, \xi, \theta) \sigma_{ns}^{(0)}(\zeta) \rho_{n sr}^{(0)}(\theta) + \dots \quad (36)$$

And the energy to the fourth order

$$W_{n sr} = V_n^{(0)} + \kappa^2 W_{ns}^{(2)} + \kappa^4 W_{n sr}^{(4)} + \dots \quad (37)$$

Here we see that this somewhat laborious iterative approximation has given us an elegant solution which includes corrections in the energy up to fourth order in κ ($\mathcal{O}(10^{-3})$), has illuminated the electronic system energies as a potential

energy surface (PES) for the nuclear motion, additionally we have shown that relative nuclear coordinates must be chosen at minima of this PES and at least up to this order we have separated the electronic, nuclear vibrational, and nuclear rotational wave functions. This concludes the derivation, the remainder of the original article includes application of these results to calculate transition probabilities and solve the particular example of a diatomic molecule instead of reviewing that we will look at applying this to solids.

4 Further Development: Translation from Molecules to Solids

Nearly 30 years after the publication of the Born Oppenheimer approximation, Born along with Kun Huang published the book *Dynamical Theory of Crystal Lattices* [3] in which the Born Oppenheimer approximation is carried out and discussed in the context of solids. Everything essentially follows the method laid out in sec. 3 because all of the terms in the Hamiltonian were left general so this is essentially extending that treatment by treating a solid as a molecule with a very large number of ions and electrons to sum over.

They again start with the assumption that the nuclear motion is much slower than the electron motion to solve the zeroth order equation for the electronic energies and wave functions at fixed nuclear positions. This is treated as a solved problem in this text but can be solved with one of the standard methods such as tight binding, weak periodic potential, or any of the more accurate methods discussed in chapter 11 of A&M [1]. For solids the approximation is typically broken off at the second order equation, since this is where the harmonic equation for the ionic motion is introduced as seen in eq. 26 this is typically referred to as the *harmonic approximation*. In the harmonic approximation the wave function is determined up to the zeroth order and is the product of the electronic wave function, $\phi_n^0(x; \xi_0)$, and the ionic motion, $\chi^{(0)}(\zeta)$.

The 6 coordinates describing the net translation and rotation of the total configuration, θ_i , don't contribute in a solid because total system translations don't effect the result and the rotational terms are proportional to the moment of inertia of the ionic system so with the number of ions in a solid very large these terms become negligibly small. It is mentioned that if parts of the solid (i.e. the system of basis atoms in a unit cell) are allowed to rotate then these terms can't be ignored and will produce degeneracies but this possibility isn't covered here.

The harmonic approximation breaks down for higher order terms but the method can continue to be used up to the second order in the wave function namely:

$$\psi_n(x, \zeta) = \left(\chi^{(0)}(\zeta) + \kappa \chi^{(1)}(\zeta) + \kappa^2 \chi^{(2)}(\zeta) \right) \phi_n(x, \xi_0) \quad (38)$$

If you extend the approximation beyond this to the third order in the wave function or fifth order in the Hamiltonian the wave functions contain terms of the form $F(x, \xi)$ which no longer depend on x solely through functions of $\phi_n^{(r)}$ so

the electronic motion is no longer separable from the nuclear motion. Because of this the expansion is truncated to the second order or below in the wave function and fourth order or below in the Hamiltonian is considered the *adiabatic approximation* which we will discuss some implications of it's breakdown and ways to extend its validity in [sec. 5](#).

4.1 Harmonic Approximation from B-O in Solids

For the harmonic approximation described in the preceding sections we will follow the notation from Born and Huang [3] where the potential function for the nuclei defined by a specific electronic state is given by Φ (given by $V_n^{(2)}$ in [sec. 3.3](#)) and a new notation for derivatives is introduced:

$$\Phi_\alpha(k) = \left(\frac{\partial \Phi}{\partial x_\alpha(k)} \right)_0 \quad (39)$$

and

$$\Phi_{\alpha\beta}(k, k') = \left(\frac{\partial^2 \Phi}{\partial x_\alpha(k) \partial x_\beta(k')} \right)_0 \quad (40)$$

Where k indexes the ion with mass m_k and $\alpha = 1,2,3$ indexes the three rectangular coordinates. The subscript 0 denotes that these are evaluated at the mean nuclear location $x_\alpha^0(k)$ (upper and lower case distinction has been dropped since we are just concerning ourselves with nuclear motions here) which are determined by the condition found from the first order equation in the B-O approximation, $\Phi_\alpha(k) = 0$. With this notation the effective potential function is

$$\Phi = \frac{1}{2} \sum_{kk'} \sum_{\alpha\beta} \Phi_{\alpha\beta}(k, k') u_\alpha(k) u_\beta(k') \quad (41)$$

Where u is the small displacement from the mean nuclear positions (previously denoted by ζ). We can redefine Φ and u to remove the mass dependence by constructing the new matrix, called the dynamical matrix defined as

$$D_{\alpha\beta}(k, k') = \frac{1}{(m_k m_{k'})^{\frac{1}{2}}} \Phi_{\alpha\beta}(k, k') \quad (42)$$

and by constructing the new displacements

$$\omega_\alpha(k) = m_k^{\frac{1}{2}} u_\alpha(k) \quad (43)$$

The Hamiltonian is now:

$$H = \frac{1}{2} \sum_k \sum_\alpha P_\alpha^2(k) + \frac{1}{2} \sum_{kk'} \sum_{\alpha\beta} D_{\alpha\beta}(k, k') \omega_\alpha(k) \omega_\beta(k') \quad (44)$$

Where $P_\alpha(k)$ is the conjugate momentum to the $\omega_\alpha(k)$ displacements. The dynamical matrix couples the coordinates, $\omega_\alpha(k)$, so we can transform to normal

coordinates that form an orthogonal set for this Hamiltonian, q_j . These are defined by

$$q_j = \sum_k \sum_\alpha e_\alpha(k|j) \omega_\alpha(k) \quad (45)$$

One can look in the original reference for the details on how to determine the transformation coefficients $e_\alpha(k|j)$ but once you've converted to these coordinates you are left with a Schrodinger equation of the form:

$$\frac{1}{2} \sum_j (P_j^2 + \omega_j^2 q_j^2 - \epsilon_j) \chi = 0 \quad (46)$$

Where again P_j is the conjugate momentum to the normal coordinates, q_j . Transforming to normal coordinates has left us with a Hamiltonian that is just a sum of terms each dependent on only one coordinate so the nuclear wave function can be separated as:

$$\chi = \chi_1(q_1) \chi_2(q_2) \dots \chi_{3N}(q_{3N}) \quad (47)$$

And the total energy, ϵ , is just

$$\epsilon = \sum_{j=1}^{3N} \epsilon_j \quad (48)$$

This is just the equation for $3N$ quantum harmonic oscillators which have energies:

$$\epsilon_i = \hbar \omega_j \left(\nu_j + \frac{1}{2} \right) \quad (49)$$

From this we see that the harmonic approximation that came from truncating the Born-Oppenheimer approximation in solids at the second order in the Hamiltonian gives us a formalism for determining the phonon spectrum and dispersion relation in a solid. This is a useful treatment but in practice there are many cases in which you need to include anharmonic terms in order to accurately determine properties of a solid. I will also show that the adiabatic approximation can be extended further than the harmonic approximation but that there are also some important cases in which even this approximation breaks down and the simplicity that follows from these key assumption in the Born-Oppenheimer approximation is lost.

5 Further Development: Extensions and Failures of the Harmonic Adiabatic Approximation

The adiabatic approximation requires that κ is small which is always true but it also assumes that the electron-phonon coupling coefficient is also small. This

latter assumption is not as obvious and requires more careful treatment. Born and Huang [3] point this out without going into any real detail in appendix VII but a number of others [6][5][7] have followed up this problem and have given methods for extending the adiabatic approximation including terms in the Hamiltonian for the electron-phonon coupling. Here we will follow some of these papers and show some of the repercussions.

Important conclusions are that the key parameter for the validity of these adapted expansions will be ω_{max}/ϵ_F or similarly V_k/ϵ_F where ω_{max} is the maximum phonon frequency, V_K are the fourier components of the new effective potential including the electron-phonon coupling at the points of the reciprocal lattice K . Physically the main conclusion is that this method does not do a good job of describing the dynamics of the electronic system in a shell of states around the fermi energy so quantities that rely on the dynamics of these electrons such as specific heat and spin magnetic susceptibility will not be well described by this approximation while quantities that rely on the bulk dynamics of all of the electrons and ions in the system such as cohesive energy and the normal modes can be determined to good accuracy with this method.

The Born Oppenheimer approximation takes the electrons and ions as decoupled but if these were truly decoupled in metals the resistance would tend to be very large because of the long range of the ionic coulomb potentials and the longitudinal lattice vibrations would tend toward the plasma frequency instead of to 0 for small k . Both of these are not observed for normal metals so a more accurate picture would be to expect that the majority of the electrons tend to follow the ions and effectively screen the electron-electron and electron-ion coulomb potential.

To demonstrate this we will explicitly break out the adiabatic and non-adiabatic terms to see how large they are relative to one another and determine which electrons in the system contribute dominantly to each of these terms. For this we add to the Schrodinger equation for the ionic motion electron-ion coupling terms:

$$(T_N + \Phi_n(X) - E)\psi_n(X) + \sum_{n'} C_{nn'}(X, P)\psi_{n'}(X) \quad (50)$$

where $\Phi_n(X)$ can be taken as the function determined from the electronic Hamiltonian at fixed ion positions and can include the ion-ion potential and the electron-ion interaction $C_{nn'}$ is the electron phonon coupling matrix and is given by:

$$C_{nn'} = \sum_k \frac{1}{M_k} (A_{nn'}^{(k)} P_k + B_{nn'}^{(k)}) \quad (51a)$$

$$A_{nn'}^{(k)}(X) = \int \phi_n^*(x, X) P_k \phi_{n'}(x, X) dx \quad (51b)$$

$$B_{nn'}^{(k)}(X) = \frac{1}{2} \int \phi_n^*(x, X) P_k^2 \phi_{n'}(x, X) dx \quad (51c)$$

Noting that the diagonal components of $A_{nn'}$ integrate to zero, the Hamiltonian can be written to separate the adiabatic and nonadiabatic terms as

$$H_{nn'} = (T_N + \Phi_n(X) + B_{nn})\delta_{nn'} + C_{nn'} \quad (52)$$

We can take only the diagonal terms which give us an adiabatic eigensystem for which we can treat the non-adiabatic terms as a small perturbation. The leading order correction in the ionic wave function is

$$\delta\chi_{mn} = \sum_{n'} \frac{C_{nn'}\chi_{mn'}^{(0)}}{E_n - E_{n'}} \quad (53)$$

It can be shown ([7] Appendix 1) that the order of $C_{nn'}$ is $\sim \hbar\bar{v}/l$ where \bar{v} is the average ionic velocity and l is the ionic displacement required to produce a change in the electronic wave function. Since $C_{nn'}$ only connects states n to states $n \pm 1$ and pauli exclusion restricts the available states to those near the fermi energy so that the denominator will be of order ϵ_F . The states that we need to be careful about here are those just above and below the fermi energy because although there are not many of these states the nonadiabatic terms for these states do produce important contributions to some key properties of solids such as spin paramagnetism and specific heat. These states that we need to treat nonadiabatically live in the shell about the fermi energy of approximate thickness:

$$|E_n - E_{n'}| \sim \hbar\bar{v}/l \leq \hbar\omega_{max} \quad (54)$$

To find the change in energy δE due to the nonadiabatic terms we recast using second quantization notation and apply second order perturbation theory for A and first order perturbation theory for B then renormalize. The methods at this point starts to dip into field theoretical methods that surpass my math and physics training so I will avoid going into detail but I will try to capture some of the key results discussed after following this procedure.

The cohesive energy which we have said isn't strongly dependent solely on the states around the fermi energy can be written as

$$\mathcal{E}_0 = E_0 + \sum \frac{1}{2}\hbar\omega_f + \Delta E \quad (55)$$

Where E_0 is the lowest electronic energy for the fixed ion problem, $\sum \frac{1}{2}\hbar\omega_f$ is the zero point energy for the lattice and ΔE is the correction from the nonadiabatic terms. This term is on the order of

$$\Delta E \sim (m/M)^{1/2} \sum_F \frac{1}{2}\hbar\omega_f \quad (56)$$

which is indeed small.

Next we look at the specific heat, a quantity that we believe should be more sensitive to electrons near the Fermi surface. We get the lowest order correction to the temperature dependence of the free energy by only including the electrons

in a shell withing kT of the Fermi energy. This gives a correction approximately proportional to:

$$F^C \simeq \sum_k \frac{\bar{n}_k(1 - \bar{n}_{k-f})}{(\hbar\bar{\omega})^2} |v_f|^2 \quad (57)$$

where n is the standard occupation number and $\bar{\omega}$ is an average value of ω the phonon frequencies. Because the denominator can be quite small this term can be quite large. Roughly this term is of the magnitude $C(kT/\epsilon_F)^2$, some reasonable electron phonon coupling strengths are $\sim (\frac{1}{8} - 1)\epsilon_F$ so this term is roughly the same order as the unperturbed free energy $\sim \epsilon_F(kT/\epsilon_F)^2$.

Additionally, we can look for evidence of the importance of electron phonon coupling outside of calculating terms through this expansion framework. We can look to experiment and more realistic calculation methods that don't require adiabatic approximations. In these cases it is shown that electron phonon coupling is significant in describing ballistic transport [10], low temperature superconductivity [2], high temperature superconductivity [9], and key physical parameters in carbon structures (graphene, nanotubes). A particularly nice case to look at is that of graphene where electron phonon coupling has been shown to produce kinks in the phonon dispersion due to Kohn anomalies (coupling of electron states k_1 and $k_2 = k_1 + q$ both on the fermi surface with phonon wavevector q) and line broadening in the raman spectra due to optical phonon coupling. These give experimental methods for determining the electron phonon coupling strength. Using this method Ferrari [8] reports electron phonon coupling strength in graphene $\sim (39-47 \text{ eV/\AA})^2$, clearly demonstrating the importance of including nonadiabatic interactions in this system.

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