Nearsightedness of Electronic Matter

E. Prodan\textsuperscript{1,2} and W. Kohn\textsuperscript{1}

\textsuperscript{1}Dept. of Physics, University of California, Santa Barbara, CA 93106 and
\textsuperscript{2}Dept. of Materials Science, University of Southern California, Los Angeles, CA 90089

In an earlier paper, W. Kohn had qualitatively introduced the concept of “nearsightedness” of electrons in many-atom systems. It can be viewed as underlying such important ideas as Pauling’s “chemical bond,” “transferability” and Yang’s computational principle of “divide and conquer.” It describes the fact that, for fixed chemical potential, local electronic properties, like the density $n(r)$, depend significantly on the effective external potential only at nearby points. Changes of that potential, no matter how large, beyond a distance $R$ have limited effects on local electronic properties, which rapidly tend to zero as function of $R$. In the present paper, the concept is first sharpened for representative models of uncharged fermions moving in external potentials, followed by a discussion of the effects of electron-electron interactions and of perturbing external charges.

PACS numbers: 71.10.-w, 71.15.-m

It is a conventional qualitative wisdom among physicists and chemists that, in the absence of long range ionic interactions, if an atom A in a solid is exchanged for another atom B, the change of the total energy of the system is largely determined by atoms A and B and their near neighbors. Similarly for a molecule M adsorbed on a surface. These are qualitative examples of “nearsightedness.”

Understanding the physics and chemistry of large molecules and solids would have been practically impossible if not for the principle of transferability \cite{1,2}. It is generally accepted that, in the absence of long range ionic interactions, large molecules or materials systems can be studied and understood one neighborhood at a time, without the necessity of studying the entire system at once. The useful computational method of “divide and conquer” takes advantage of this fact \cite{3}.

We can argue that Pauling’s concept \cite{4} of the chemical bond has a well defined meaning because, to a good approximation, its properties depend only on the relative positions of the bonded atoms and their near neighbors \cite{5}. Anything beyond them, has little influence on the properties of the chemical bond.

These important concepts, based on decades of empirical and computational work, point to a property of matter which we call “nearsightedness of electronic matter (NEM).” It was first realized and introduced by one of the authors (WK) in 1996 \cite{6}. In retrospect, one can find precursors of NEM implicit in many other contexts: For example, in the work of Thomas and Fermi in the 1920’s \cite{7}: in the proposal of the Local Density Approximation in 1965 \cite{8} and in Yaniv and Kohn’s paper of 1979, “Locality Principle in Wave Mechanics” \cite{9}. It was also noticed in Lang and Kohn’s extensive work on surfaces \cite{10} and as an element of the concept of “edge electrons” in Ref. \cite{11}.

NEM deals with the following scenario: We consider an unperturbed system of very many charged or uncharged electrons in equilibrium in an external, static potential $v(r)$, with chemical potential $\mu$, at $T = 0^+$. We are interested in the effect (for fixed $\mu$) of a perturbing potential (change of the external potential) $w(r')$, of finite support (footprint) \cite{12}, on a local property at a point $r_0$, like the density $n(r_0)$, when the support of $w(r')$ is outside a sphere of radius $R$, centered at $r_0$ (Fig. 1). The NEM principle states that, for a given unperturbed system and a given $R$, the density changes at $r_0$, $\Delta n(r_0)$, due to all admissible $w(r')$, have a finite maximum magnitude, $\Delta n$, which, of course, depends on $r_0$, $R$, and on the unperturbed system. From this definition, one can see that $\Delta n(r_0, R)$ decays monotonically as a function of $R$. In this paper we prove, for broad classes of systems, that in fact,

$$\lim_{R \to \infty} \Delta n(r_0, R) = 0, \quad (1)$$

and expect this to be valid very generally. We shall show that, for ordered gapless systems, the decay follows power-laws, for ordered gapped systems the decay is exponential and for disordered, gapped or ungapped systems, the decay is also exponential.

For a given $r_0$ and $\Delta n$, we can solve for $R$ from $\Delta n(r_0, R) = \Delta n$ and hence define what we call the nearsightedness range $R(0, \Delta n)$. The significance of $R(0, \Delta n)$ is the following: the density changes at $r_0$ due to any perturbation, of arbitrary shape and amplitude, beyond $R(0, \Delta n)$, cannot exceed $\Delta n$. We can say, anthropomorphically that, to within an accuracy $\Delta n$, the particle density $n(r)$ cannot “see” any perturbation $w(r')$ beyond the distance $R(r_0, \Delta n)$; hence our word “nearsightedness.”

NEM frequently reminds of other well known and well understood concepts but, in fact, is different. To avoid “deadly sins,” let us present a list of what NEM is not:

1) NEM is not an aspect of linear or higher order nonlinear response to external perturbations (but does not exclude these).

2) NEM is not screening of charges, which renders long
range Coulomb potentials short range (NEM applies also to neutral fermions).

3) NEM does not apply to systems of few electrons or to non-interacting bosons below their condensation temperature (interacting bosons are beyond the scope of this paper).

4) NEM is not limited to electrons at \( T = 0^+ \) but carries over to finite \( T \), including the classical (high \( T \)) limit.

5) NEM is not limited to macroscopically homogeneous systems. E.g., it applies to a point \( r \) on an interface.

In this article, we communicate the first quantitative results on NEM for 1, 2 and 3D non-interacting, periodic electrons and preliminary results for non-periodic and interacting electrons. We shall see that, no matter how complicated or strong \( w(r') \) is, far away from the perturbation, the change of electron density has a universal form, which is completely determined by the reflection coefficient, in 1D, or elements of the scattering matrix, in 2 and 3D, evaluated at certain energies. NEM follows from the fact that these coefficients cannot exceed a certain upper bound. Based on these asymptotic estimates, we discuss the nearsighted range and present an application to linear scaling electronic algorithms.

**Non-interacting fermions:** We emphasise again that NEM, as a general principle, does not require interactions or screening. It is due to the destructive interference of density (not wave) amplitudes \( n_j \) associated with the occupied single particle eigenstates \( \psi_j \).

**One dimension:** We begin with a model of 1D electrons in a periodic potential \( v(x) \) with inversion symmetry, at \( T = 0^+ \). The unperturbed Hamiltonian is \( \left[ \hbar = 2m = 1 \right] \)

\[
H_0 = -\frac{d^2}{dx^2} + v(x), \quad v(x + b) = v(x). \tag{2}
\]

We first restrict the perturbing potential \( w(x) \) to vanish for \( x > 0 \). The density change is given by

\[
\Delta n(x) = \frac{1}{\pi i} \int_C [G_E(x,x) - G^0_E(x,x)]dE, \tag{3}
\]

where \( G^0_E \) and \( G_E \) are the unperturbed and perturbed Green’s functions, respectively, and \( C \) is a contour surrounding the eigenvalues below \( \mu \). The integral in Eq. (3) can be mapped into the complex \( k \)-plane,

\[
\Delta n(x) = 2 \int_C R(k) \psi_k(x)^2 dk, \quad x > 0, \tag{4}
\]

where \( C \) corresponds to \( C \), \( R(k) \) is the reflection coefficient from right to left and \( \psi_k(x) \) are the normalized, unperturbed Bloch functions \( \tilde{\psi}_k \).

a) **Asymptotics:** For insulators, we can and shall restrict ourselves to \( \text{Im} k \geq 0 \) and to the first Brillouin zone. We denote by \( \kappa \) the branch point that connects the highest occupied and the lowest unoccupied bands \( [14] \). For the case when \( w(x) \) generates no bound states in the insulating gap, we can choose \( \tilde{C} \) in Eq. (4) to be the contour \( C_1 \) in Fig. 2. Since \( \psi_k(x) = u_k(x)e^{ikx} \), with \( u_k(x) \) periodic of \( x \), \( \psi_k(x) \) decays exponentially with \( x \) \( \sim e^{\text{Im}kx} \) for \( \text{Im} k > 0 \) and the asymptotic behavior of \( \Delta n(x) \) comes from the points of \( C_1 \) in the immediate vicinity of \( \kappa \). Using the behavior of the Bloch functions near the branch point \( [14] \), we find

\[
\Delta n(x) \rightarrow 2R(\kappa) \left( \frac{2\pi}{x} \right)^{1/2} s_\kappa(x)^2 e^{-2qx}, \tag{5}
\]

where \( q \equiv \text{Im} \kappa \) and \( s_\kappa(x) \equiv |[k - \kappa]^{1/4}u_k(x)|_{k \to \kappa} \) is a real, periodic or antiperiodic function, \( s_\kappa(x + b) = \pm s_\kappa(x) \), depending on the band index. \( w(x) \) enters in this asymptotic form only through \( R(\kappa) \).

The sign of this \( \Delta n(x) \) is independent of \( x \) and is given by the sign of \( R(\kappa) \). The exponential decay constant \( q \) in

---

**FIG. 1:** Schematic of Nearsightedness of Electronic Matter: \( v(r) \) is the unperturbed external potential, \( w(r') \) is the perturbing potential outside a sphere of radius \( R \), which is centered on the point of interest \( r_0 \) (see text for details).

**FIG. 2:** The contours \( C_1 \) and \( C_2 \) on the Riemann sheet of the last occupied band (assumed odd here). \( C_1 \) surrounds the branch point \( \kappa \) and the corresponding branch cut (dashed line). \( C_2 \) intersects the real axis at \( k_F \) and reappears at \(-k_F \).
Eq. 4 equals that of the Wannier function of the highest occupied band \( |13\rangle \), or of the density matrix \( |13\rangle \).
In the limit of a sufficiently small insulating gap \( G \) (in units of the width \( W \) of the highest occupied band), \( q = \frac{1}{2} \sqrt{m^*G} \), where \( m^* \) is the effective mass at the top of the last occupied band \( |13\rangle \).

One can show that \(|\mathcal{R}(\kappa)|_{\text{max}} = 1\), with the maximum taken over all functions \( w(x) \) which generate no bound states in the insulating gap \( |13\rangle \). Thus, \( \Delta n(x) \) cannot exceed an upper bound, independent of \( w(x) \). If there are bound states, the asymptotic behavior of \( \Delta n(x) \), Eq. 5, may change, but NEM remains \( |13\rangle \).

For metals, we integrate Eq. 4 along the contour \( C_2 \) in Fig. 2. For large \( x \),
\[
\Delta n(x) \rightarrow \frac{2}{x} \ln |\mathcal{R}(k_F)\psi_{k_F}(x)|^2, 
\]
the slowly decaying Friedel oscillations \( |20\rangle \). Again, NEM follows from the fact that \(|\mathcal{R}(k_F)| \) cannot exceed 1, for any \( w(x) \).

For perturbed Kronig-Penney models \( |21\rangle \), we found that the asymptotic expressions Eqs. 4 and 5 set in after one or two lattice parameters.

b) Near-sightedness range \( R \): For a given \( \Delta n \), the near-sightedness range \( R(r_0, \Delta n) \) at \( r_0 \) was introduced as the smallest distance such that any scalar perturbation \( w(r') \), lying entirely outside this range, produces a density change at \( r_0 \), \( \Delta n(r_0) \), smaller than \( \Delta n \). Fully characterized, \( R \) is a function of \( r_0 \), chemical potential \( \mu \) and \( \Delta n \), and a functional of \( v(r) \).
\[
R \equiv R(r_0, [v(r')], \mu, \Delta n). 
\]
From this definition, it follows that, at every fixed \( r_0 \), \( \partial R(r_0, \Delta n)/\partial \Delta n \leq 0 \).

To calculate \( R \) at a point \( x_0 \), we need to simultaneously consider perturbing potentials \( w_{L,R} \) to the left and right of \( x_0 \). In this case, the density change at \( x_0 \) is given by the individual contributions \( \Delta n_{L,R}(x_0) \) of \( w_{L,R} \), Eqs. 6 and 7, plus multiple reflections corrections. In the limit when the distance from \( x_0 \) to \( w_{L,R} \) is large, these corrections were found exponentially small for insulators and comparable to \( \Delta n_{L,R}(x_0) \) for metals.

For insulators, the asymptotic behavior of \( R \) in the limit \( \Delta n \rightarrow 0 \), as derived from the upper bound of Eq. 5, from the above remark and from a cell-averaging of \( \Delta n(x) \), is
\[
\mathcal{R}(\Delta n) \rightarrow \frac{1}{2q} \ln \frac{\tilde{n}}{\Delta n}, 
\]
where
\[
\tilde{n} = \frac{8\sqrt{2\pi q}}{b} \int_0^b s_{\kappa}(x)^2 \, dx. 
\]
In the small gap and tight binding limits, \( \tilde{n} \) is completely determined by the exponential decay constant \( q \), \( \tilde{n} \rightarrow 4q\sqrt{2/\pi} \) and by \( \tilde{n} \rightarrow 4\sqrt{q/\pi b} \), respectively.

For metals, the upper bound of Eq. 6, with inclusion of multiple reflections and cell-averaging, leads to the following asymptotic behavior
\[
\mathcal{R}(\Delta n) \rightarrow 1/\Delta n. 
\]

c) Disorder: NEM is not limited to periodic \( v(x) \). As a first orientation, we discuss the effect of adding a small random potential
\[
v_r(x) = \lambda \sum_n \delta(x - x_n), 
\]
to the periodic potential \( v(x) \) in Eq. 2. We have calculated the averaged density-density correlation function, to the lowest order in \( \lambda \), assuming a random distribution of impurities with an average density \( n_i \) (cf. \( \tilde{22} \)). Our conclusions are as follows.

For insulators, the random potential changes the exponential decay constant \( q \) by
\[
\Delta q = -\lambda^2 \frac{24(q x)^2}{2b^2 \gamma^2} \int_0^b [s_{-\kappa}(x)s_{\kappa}(x)]^2 \, dx, 
\]
where \( \gamma = [(E_k - E_\kappa)/(k - \kappa)]_{k \rightarrow \infty} \). Two thirds of \( \Delta q \) are due to the narrowing of the gap \( G \),
\[
\Delta G = -\lambda^2 \frac{24(q x)^2}{bg} \int_0^b [s_{-\kappa}(x)s_{\kappa}(x)]^2 \, dx, 
\]
and one third is due to the fluctuations.

For metals, the random potential introduces an exponential decay in the averaged density response, with a decay constant
\[
q = n_i \lambda^2 g(\epsilon_F)^2 \frac{12\pi^4}{b} \int_0^b |\psi_{k_F}(x)|^4 \, dx, 
\]
where \( g(\epsilon_F) \) is the density of states at the Fermi energy. Thus, a small random potential increases \( R \) for insulators and decreases it for metals. We conjecture that this remains true for disorder, more generally.

Higher dimensions: We first consider, as an example, 2D fermions in a periodic potential with square symmetry. We present only the cases when the first band, assumed simple and isolated \( \tilde{23} \), is partially or completely filled. We first restrict the perturbing potential \( w(x,y) \) to vanish for \( y > 0 \) and the periodicity along the \( x \) direction to be preserved (so that \( k_x \) remains a good quantum number). The density change for \( y \rightarrow \infty \) is given by
\[
\Delta n(\tilde{r}) \rightarrow \sum_\epsilon \int_{\epsilon < \epsilon_F} S(\tilde{k}, \tilde{\kappa})\psi_\epsilon(\tilde{r})\psi_\kappa^\dagger(\tilde{r}) \, d\tilde{k}, 
\]
with \( \tilde{k} = (k_x, -k_y) \) and \( S(\tilde{k}, \tilde{\kappa}) \) the scattering matrix element between \( \tilde{k} \) and \( \tilde{\kappa} \).

a) Asymptotics: For fixed \( k_x \), the analytic structure relative to \( k_y \) of the band energy \( E_\kappa \) and Bloch function
ψ_F of the first band is completely analogous to that in 1D [14]: E_F and ψ_F have branch points of order 1 and 3, respectively, at κ_y = ±π + iq(k_z), connecting the first band with a higher band (we restrict ourselves to Imk_y ≥ 0 and to the first Brillouin zone). Their behavior near these points is the same as in 1D, namely E_F∞ behaves as a square root and ψ_F diverges as (k_y − κ_y)^−1/4 [24].

If the band is completely filled and w(r) does not generate bound states in the insulating gap, for a given k_x, the integral over k_y in Eq. [15] can be taken over a contour surrounding the branch point (as in Fig. 2) and its asymptotic behavior can be determined as in the 1D case. Thus, the integral over k_y decays exponentially, as function of y, with a rate 2q(k_x). There will be two values, ±k_y, of k_y where q(k_x) reaches its lowest value q_0. The asymptotic behavior of ∆n(r), for y → ∞, comes from the immediate vicinity of these points.

Defining β = (∂^2/q/∂^2k_x)k_x=κ_x of κ_0 ≡ (k_0^x, −π − iq_0), gives

\[ ∆n(r) → \frac{4π}{y} \sqrt{\beta} \text{Re}[S(κ_0, κ_0^*)φ_κ(κ_0^*)φ_κ(κ_0^*)e^{-2iq_0y}], \]

where φ_κ(κ_0) ≡ [k_y − κ_y/1/4e^{-iκ_0}e^{-iq_0κ_0}k_κ(κ_0)k_κ(κ_0)]κ→κ_0 is a quasi-periodic function in x and y. Again, w(r) enters in this asymptotic form only through S(κ_0, κ_0).

The exponential decay in Eq. [16] is twice as fast as the exponential decay, in the y direction, of the density matrix or of the Wannier function of the first band. |S(κ_0, κ_0)| = 1 for a hard wall and, in general, we expect it to be of order 1.

If the band is partially filled, the asymptotic behavior of ∆n(r) is determined by the two points on the Fermi surface, denoted by κ_0 = (k_0^x, k_0^y) and κ_0 = (k_0^x, −k_0^y), where the tangent to the Fermi surface is along the k_x-direction:

\[ ∆n(r) → 2\text{Im} \sqrt{-\frac{iπ}{ηy^3}} S(κ_0, κ_0^*)ψ_κ(κ_0^*)ψ_κ(κ_0^*)r, \]

with η the curvature of the Fermi surface at these points. From the unitarity of the scattering matrix, one can immediately find that |S(κ_0, κ_0)|_{max} = 1, with the maximum taken over all w(r). Thus, the asymptotic density change cannot exceed an upper bound, no matter how large the perturbing potential is.

The 3D case is analogous.

b) Nearsightedness range R: For metals, the simplest model is jellium enclosed by a spherical hard wall, for which one easily finds

\[ R(∆n) → \begin{cases} k_F/2∆n = 2.2r_n/∆n & (2D) \vspace{1mm} \\ k_F^2/2π∆n = 2.5r_n/∆n & (3D) \end{cases} \]

where n is the density of the uniform gas and r_s the Wigner-Seitz radius. For metals in periodic potentials, the ∆n dependence remains unchanged, but k_F is replaced by k_{eff} depending on the band structure and the filling.

For an insulator with square symmetry, we calculated ∆n(r_0) due to enclosing the point r_0 in four hard walls along the symmetry axes, at a distance D from r_0. The density change near r_0 is given by the sum of the changes due to each individual, infinitely extended wall, Eq. [16], plus multiple reflection corrections, which were found to be exponentially negligible in the limit D → ∞. Similarly for a 3D insulator with cubic symmetry. From Eq. [16], its 3D analog [24] and the previous remark, we find that the cell-averaged density change at r becomes less than a given ∆n for D ≥ D(∆n),

\[ D(∆n) → \frac{1}{2q_0} \ln \frac{\tilde{n}}{∆n}, \]

where \tilde{n} can be easily calculated from the band structure.

Finding an analytic expression of the nearsightedness range R for a general 2 or 3D insulator is clearly a next to impossible task. However, on the basis of the above calculations, the proof of exponential localization of 2 and 3D Wannier functions [25, 26] and of 1D generalized Wannier functions [15, 10], as well as our 1D result, Eqs. [15] and [8], we expect results of the following form for 2 and 3D insulators:

\[ R(∆n) → \frac{1}{2q_{eff}} \ln \frac{\tilde{n}}{∆n}. \]

where q_{eff} is an exponential decay constant of the density matrix and \tilde{n} ∝ q_{eff} (d = 2, 3).

c) Disorder: We expect the effects of disorder in 2 and 3D to be qualitatively similar to those in 1D.

Linear scaling: The CPU time for electronic structure calculations of a system consisting of many (N_a) atoms grows very rapidly with N_a, if the calculations are performed for the entire system at once. It has been pointed out [3, 27] that the dependence on N_a can be made linear for large N_a, by dividing the system into N_s suitable sub-systems, where N_s ∝ N_a. In Ref. [3], NEM was identified as the physical basis of linear scaling. Here, we quantify this idea.

The procedure is illustrated in Fig. 3 (a detailed discussion (including self-consistency) can be found in Ref. [27]). The system of volume V is divided into segments V_n, with overlapping buffer zones B_n. The density n(r) and contribution to the total energy of each V_n are obtained from calculations including its buffer zone. For a required accuracy ∆n, the thickness of B_n is chosen so that, when r is on the boundary of V_n, ∆n(r) ≤ ∆n, where ∆n(r) is the error due to the hard walls around B_n. An upper bound for b is given by the maximum of R(r, ∆n) on the boundary of V_n. Finally, the size of each V_n is chosen to minimize the total CPU time.

We exemplify this for “cubic” periodic systems in 1, 2 and 3D, where the V_n are all identical “cubes” of edge size
The system is divided into smaller volumes $V_n$ (9 in this example), with buffer zones $B_n$ (gray color).

a. The largest density change occurs at the “corners” of $V_n$ and comes primarily from the nearest walls. For metals, Eqs. (13), (14) and their 3D analog, plus the inclusion of the multiple reflections, lead to $b \rightarrow \chi r_s (\tilde{n}/\Delta n)^{2/(d+1)}$, with $\chi = 0.31, 0.91$ and 1.0 for 1, 2 and 3D, respectively. For a 5% accuracy, $b = 6.2, 6.7$ and 4.5$r_s$, respectively. Similarly, for insulators, $b \rightarrow (2\nu_0)^{-1} \ln(\tilde{n}/2\Delta n)$, with $\tilde{n}$ defined in Eqs. (16) and (19).

The total CPU time is given by $t = N_a \tau$, where $N_a (= V/a^d)$ is the number of segments, and $\tau \propto (2b + a)^{vd}$ is the CPU time for the electronic structure calculation of one segment plus its buffer zone [$\nu = 2 - 3$ for DFT [27], and higher for other methods]. Minimizing the total CPU time with respect to $a$, we obtain the optimal size, $a = 2b/(\nu - 1)$. With this optimization, and from our estimates of $b$, we obtain the following dependence of the total CPU time on the desired accuracy and the total number of atoms:

$$t \propto N_a \times \begin{cases} \Delta n^{2(1-v)d/(d+1)} \quad &\text{(ungapped)} \\ \ln(\tilde{n}/2\Delta n)^{(\nu-1)d} \quad &\text{(gapped)} \end{cases}$$  (21)

For metals, $b$ can be greatly reduced by averaging the wall-induced Friedel oscillations over two or more values of $b$.

**Interacting fermions:** In considering the response of charged fermions to distant disturbances it is necessary to distinguish between two cases:

a) Distant perturbing potentials $w(r')$, with $|r_0 - r'| \geq R$. The simplest description of many-body interaction effects is the random phase approximation which, in all dimensions, leads to a decrease of $R$ in typical metals but an increase of $R$ in typical insulators due to a reduction in the gap $\Delta$.

b) Distant perturbing charge densities $\rho(r')$. In analogy with $R(r_0, \Delta n)$, we define a charge-nearsightedness range, $R_n(r_0, \Delta n)$ as the smallest distance such that any charge perturbation $\rho(r')$ lying entirely outside this range produces a density change at $r_0$, $\Delta n(r_0)$, smaller than $\Delta n$.

As is well known, the long range Coulomb potential, due to perturbing electric charges, is screened out by metallic electrons. Preliminary model calculations for metallic electrons, in the Thomas-Fermi approximation, indicate that they are charge-nearsighted, i.e. have a finite $R_n$. However, charged insulating fermions are "classically farsighted," in the sense that, at sufficiently large distances, the fermions “see” the classical long range total potential $\int \rho(r')/|r_0 - r'| dr'$, were $\rho_i$ is the total perturbing charge density, including depolarization. Thus, for example, in metals, replacing a neutral atom or ion by another atom or ion has always short range electronic consequences, while, in an insulator, ions lead to classical long range electronic effects.

This work was supported by Grants No. NSF-DMR03-13980, NSF-DMR04-27188 and DOE-DE-FG02-04ER46130. One of us (W.K.) gratefully acknowledges the frequent hospitality of the Institute for Theoretical Physics of the ETH, Zurich, and stimulating discussions with Prof. J. Friedel.

[1] Levy, M., et al (1974) J. Chem. Phys. 61, 1844.
[2] Allen, T.L. and Suhll, H. (1961) J. Chem. Phys. 35, 1644.
[3] Yang, W. (1991) Phys. Rev. Lett. 66, 1438.
[4] Pauling, L. (1967) The chemical bond: Cornell Univ. Press, Ithaca, NY.
[5] Allen, T.L. (1959) J. Chem. Phys. 31, 1039.
[6] Kohn, W. (1996) Phys. Rev. Lett. 76, 3168.
[7] Fermi, E. (1927) Rend. Accad. Naz. Lincei 6, 602; Thomas, L.H. (1927) Proc. Camp. Philos. Soc. 23, 542.
[8] Kohn, W. and Sham, L.J. (1965) Phys. Rev. 140, A1133.
[9] Kohn, W. and Yaniv, A. (1978) Proc. Nat. Acad. Sci. 75, 5270.
[10] Lang, N.D. and Kohn, W. (1970) Phys. Rev. B 1, 4555.
[11] Kohn, W. and Mattsson, A.E. (1998) Phys. Rev. Lett. 81, 3487.
[12] The set of points, limited to a finite region, where $w(r') \neq 0$.
[13] Prodan, E., cond-mat/0506687
[14] Kohn, W. (1959) Phys. Rev. 115, 809.
[15] Kohn, W. and Onufroy, J.R. (1973) Phys. Rev. B 8, 2485.
[16] Rehr, J.J. and Kohn, W. (1974) Phys. Rev. B 10, 448.
[17] Pei, C. (1977) Contributions to the Electronic Theory of Solid Interfaces, PhD. Thesis, Univ. of California.
[18] He, L. and Vanderbilt, D. (2001) Phys. Rev. Lett. 86, 5341.
[19] Since $m^* \propto \sqrt{q}$, $q \propto G$, in line with Beigi, S.I. and Arias, T.A. (1999) Phys. Rev. Lett. 82, 2127.
[20] Friedel, J. (1952) Philosophical Magazine 43 153.
[21] R. de L. Kronig and Penney, W.G. (1931) Proc. Roy. Soc. A130.
[22] Edwards, S.F. (1958) Philos. Magazine 3, 1020.
[23] Non-degenerate and with convex iso-energetic lines in $k$-
space.
[24] Prodan, E. and Kohn, W., to be published.
[25] des Cloizeaux, J. (1964) Phys. Rev. 135, A698.
[26] Heine, V. (1963) Proc. Phys. Soc. (London) 81, 300.
[27] Wo, S.Y. and Jayanthi, C.S. (2002) Phys. Rep. 358, 1.