CONDENSED MATTER THEORY: FROM MODELS TO FIRST PRINCIPLES

MARVIN L. COHEN
Department of Physics, University of California, and Materials Sciences Division, Lawrence Berkeley Laboratory
Berkeley, CA
IT WAS SUGGESTED THAT I

“REVIEW CMT WITH EMPHASIS ON ELECTRONIC STRUCTURE AND THE DEVELOPMENT OF COMPUTATIONAL METHODS TO CALCULATE AND PREDICT PROPERTIES OF REAL MATERIALS AND GIVE MODERN EXAMPLES (MY OWN WORK)”
IT WAS SUGGESTED THAT I

“REVIEW CMT WITH EMPHASIS ON ELECTRONIC STRUCTURE AND THE DEVELOPMENT OF COMPUTATIONAL METHODS TO CALCULATE AND PREDICT PROPERTIES OF REAL MATERIALS AND GIVE MODERN EXAMPLES (MY OWN WORK)”

ALL MY REJECTION LETTERS FROM PRL
IT WAS SUGGESTED THAT I

“REVIEW CMT WITH EMPHASIS ON ELECTRONIC STRUCTURE AND THE DEVELOPMENT OF COMPUTATIONAL METHODS TO CALCULATE AND PREDICT PROPERTIES OF REAL MATERIALS AND GIVE MODERN EXAMPLES (MY OWN WORK)”

NANOSCIENCE AND SUPERCONDUCTIVITY
PREHISTORY

EINSTEIN, DIRAC,
SOMMERFELD-BETHE, FERMI
EINSTEIN 1905

DETERMINATION OF MOLECULAR DIMENSIONS

BROWNIAN MOTION

SPECIAL RELATIVITY

PHOTOELECTRIC EFFECT
Figure 3 Comparison of experimental values of the heat capacity of diamond with values calculated on the Einstein model, using the characteristic temperature $\Theta_E = \frac{\hbar \omega}{k_B} = 1320^\circ\text{K}$. [After A. Einstein, Ann. Physik 22, 180 (1907).]

This figure is still in textbooks after a century.
Dirac (1929)

"The underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

BRILLOUIN ZONES
SOMMERFELD AND BETHE 1933
PSEUDOPOTENTIAL - FERMI 1934

All'esterno della buca, dove \( V(r) \) si annulla, la \( u \) è dunque una funzione lineare di \( r \). E siccome il valore di \( \psi \) lontano dalla buca deve tendere approssimativamente al valore \( \tilde{\psi} \), si potrà porre, all'esterno della buca:

\[
(11) \quad u(r) = (a + r) \tilde{\psi}
\]
dove \( a \) è una lunghezza, il cui significato è chiarito nella Fig. 1. In essa sono riportati in ascisse i valori di \( r \) e in ordinate quelli di \( u \). La \( u \), come risulta dalla (9), è nulla per \( r = 0 \), mentre, per \( r \) maggiore di \( \rho \) ha per grafico una retta. Prolunghiamo questa retta fino ad incontrare l'asse delle ascisse; \( \rho \) è la distanza del punto di intersezione dall'origine delle coordinate.

Tenendo conto di (9), (10) e (11) troviamo

\[
(12) \quad \frac{8\pi^2 m}{\hbar^2} \int V \psi \delta r = 4\pi \frac{8\pi^2 m}{\hbar^2} \int u \delta r = 4\pi \int u'' \delta r
\]

\[
= 4\pi |u'| r - u'| = -4\pi a \tilde{\psi}
\]
e siccome nell'unità di volume sono contenute \( n \) buche di potenziale, ricaviamo infine

\[
(13) \quad \frac{8\pi^2 m}{\hbar^2} \Delta \psi = -4\pi a \tilde{\psi}.
\]

Con ciò la (8) diventa

\[
(14) \quad \Delta \psi + \frac{8\pi^2 m}{\hbar^2} (W_u - U) \psi = 0
\]
dove si è posto

\[
(15) \quad W_u = W + \frac{\Delta m}{2m},
\]

DENSITY FUNCTIONAL THEORY - DIRAC 1930
1940-1960

HERRING-SLATER-PHILLIPS
1957--PRL, BCS, but no accurate/detailed Si E(k)
1957--PRL, BCS, but no accurate/detailed Si $E(k)$

BUT BY...

1965--14 accurate semiconductor $E(K)$’s-EPM
1970--optical structure of semiconductors solved
1980’s--structural properties, superc., surf., high P
1990-2008 --complex materials, nanostructures, and a variety of properties
“I'm often asked whether doing physics research using computers is ‘mindless research.’ My answer is that I can do ‘mindless research’ without a computer.”

M. L. Cohen (1970)
For calculating materials properties: “If given the choice between the computers of today together with the physical concepts of the 1970's—or—the computers of the 1970's along with current concepts, I'd choose the latter.”

J. R. Chelikowsky (2000)
CONCEPTUAL BASIS

ONE CAN ARGUE FOR TWO MODELS OR “MENTAL PICTURES” OF A SOLID:

“INTERACTING ATOMS”

and

“ELEMENTARY EXCITATIONS” MODELS
INTERACTING ATOMS MODEL

A solid is a collection of strongly interacting atoms.

The particles are electrons and nuclei interacting via EM interactions.

(associated with reductionism)
ELEMENTARY EXCITATION MODEL

particles are mainly: quasiparticles and collective excitations [probe-response] (emergent behavior)

quasiparticles: quasielectrons (like polarons), holes, superconducting quasiparticles,…

collective excitations: phonons, plasmons, magnons,…
Standard Model
Plane Wave Pseudopotential Method
[PWPM]
3s Radial Wavefunction of Si

Radial distance (a.u.)
Charge Density of Si
<table>
<thead>
<tr>
<th></th>
<th>lattice constant (Å)</th>
<th>bulk modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>calc. 5.45</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>expt. 5.43</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>% diff. 0.4%</td>
<td>1%</td>
</tr>
<tr>
<td>Ge</td>
<td>calc. 5.66</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>expt. 5.65</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>% diff. 0.1%</td>
<td>-5%</td>
</tr>
<tr>
<td>C</td>
<td>calc. 3.60</td>
<td>441</td>
</tr>
<tr>
<td></td>
<td>expt. 3.57</td>
<td>443</td>
</tr>
<tr>
<td></td>
<td>% diff. 0.8%</td>
<td>-1%</td>
</tr>
</tbody>
</table>
Plane Wave Pseudopotential Method

(Standard Model of Solids)

For a broad class of solids, clusters, and molecules, this method describes ground-state and excited-state properties such as:

- electronic structure
- crystal structure and structural transitions
- structural and mechanical properties
- vibrational properties
- electron-lattice interactions
- superconductivity
- optical properties
CONFINEMENT
REDUCED DIMENSIONALITY
SYMMETRY
Nanotubes are indexed by the circumferential periodicity.

The \((3,5)\) nanotube.
2-D graphene as physical realization of (2+1)D QED

Single particle energy dispersion

Massless Dirac equation with $c^* \sim c/300 \sim 10^6 \text{m/s}$

Quantum Hall effect in graphene observed

Electric field induced half-metallic states in graphene nanoribbons

Effect of Transverse Electric Field on Edge States

- Spin polarization of carriers is 100%.
- It is tunable and reversible!
- Electric field is more effective on wider nanoribbons ($E_c \sim 1/w$)
(8,0)/(7,1) Nanotube Schottky Barrier

Chico, Crespi, Benedict, Cohen & Louie, PRL (1996)
Sensor Concept: Sensing Specific Analytes

Architecture:
integration of three layers

1. Recognition layers or recognition molecules to achieve analyte specificity
2. NTFET as transducer
3. Si CMOS architecture
Boron Nitride Nanotubes

Predicted by theory
Semiconductors
Electronic properties independent of tube chirality

CLASSES OF SUPERCONDUCTORS

-----------------------------

BCS : conventional metals, C60, some organics, doped semiconductors, MgB2,…

-----------------------------

“BCS” EXOTIC: copper oxides, heavy fermion metals, some organics,…
Can BCS theory predict $T_c$?

$$T_c \sim T_D e^{-\frac{1}{NV}} \approx 11K$$

If "$NV \rightarrow 0.03\ T_c \rightarrow 10^{-12}\$

Need to know "$NV\" very accurately to predict $T_c$.

Doped semiconductor

Sr Ti O$_3$

First superconducting oxide

(Cohen 1963; Schooley et al 1964)
Superconductivity in the Eliashberg Formalism

BCS Theory

Main ingredient: momentum– and frequency-dependent
Eliashberg function

\[ \alpha^2 F(\vec{k}, \vec{k}', \omega) \equiv N(\varepsilon_F) \sum_j |g_{j\vec{k}\vec{k}'}^j|^2 \delta(\omega - \omega_{j\vec{q}}) \]

where \( N(\varepsilon_F) = \) density of states per spin at Fermi level
\( g_{j\vec{k}\vec{k}'} = \) electron-phonon matrix element
\( \omega_{j\vec{q}} = \) frequency of phonon in jth branch with \( \vec{q} = \vec{k} - \vec{k}' \)

Equivalently:

\[ \lambda(\vec{k}, \vec{k}', n) = \int_0^\infty d\omega \alpha^2 F(\vec{k}, \vec{k}', \omega) \frac{2\omega}{\omega^2 + (2n\pi T)^2} \]

\[ \lambda = <\lambda(\vec{k}, \vec{k}', 0)> \]
sh and hcp SILICON Tc (Pressure)

\[ T_c (K) \]

\[ \text{PRESSURE (GPa)} \]

**THEORY**
CHANG, DACOROGNA & COHEN

**EXP.**
GRENOBLE: MIGNOT, CHOUTEAU & MARTINEZ
BERKELEY: ERSKINE & YU
Transition Temperature and Isotope Effect

<table>
<thead>
<tr>
<th></th>
<th>harmonic</th>
<th></th>
<th>anharmonic</th>
<th></th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>isotropic</td>
<td>anisotropic</td>
<td>isotropic</td>
<td>anisotropic</td>
<td></td>
</tr>
<tr>
<td>$T_c$</td>
<td>28 K</td>
<td>55 K</td>
<td>19 K</td>
<td>39 K</td>
<td>39 K</td>
</tr>
<tr>
<td>$\alpha_B$</td>
<td>0.42</td>
<td>0.46</td>
<td>0.25</td>
<td>0.32</td>
<td>0.26, 0.30</td>
</tr>
<tr>
<td>$\alpha_{Mg}$</td>
<td>0.04</td>
<td>0.02</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.73</td>
<td></td>
<td>0.61</td>
<td></td>
<td>0.58, 0.62</td>
</tr>
<tr>
<td>$\omega_{ph}$</td>
<td>62.7 meV</td>
<td></td>
<td>75.9 meV</td>
<td></td>
<td>75.9, 76.9</td>
</tr>
</tbody>
</table>

$\mu^*(\omega_c) = 0.12$.

$\lambda$ : averaged electron-phonon coupling.

$\omega_{ph}$ : frequency of the in-plane B–B stretching modes ($E_{2g}$) at $\Gamma$.

For $0.10 \leq \mu^*(\omega_c) \leq 0.14$, $41 \text{ K} \geq T_c \geq 37 \text{ K}$
Superconducting Gap at 4K

- $\Delta(k)$ on Fermi surface at $T=4$ K

- Large gap on cylindrical $\sigma$–sheets

- 2 dominant sets of gap values
RAISING $T_c$

WE TRIED TO USE THEORY TO SUGGEST HOW TO INCREASE THE TRANSITION TEMPERATURE OF MAGNESIUM DIBORIDE SIGNIFICANTLY BUT FAILED!

THIS RESULT IS CONSISTENT WITH EXPERIMENTS UP TO NOW.
\( \frac{T_c}{T_0} \approx 0.69 e^{-\frac{1}{\chi - \chi^*}} \)

Kresin-Barbee-Cohen
\[ \frac{T_c}{\langle \omega \rangle} = 0.26 (E_{\chi}^* - 1)^{-1} \]

McMillan 1968

\[ M^* = 0 \]
ELECTRON-PHONON COUPLING

$$\lambda \langle \omega^2 \rangle = \sum_i \frac{\eta_i}{M_i}$$

SO $\lambda$ CAN BE VIEWED AS THE RATIO OF AN ELECTRONIC SPRING CONSTANT $\eta$ AND A LATTICE SPRING CONSTANT
Superconductivity in diamond

E. A. Ekinov¹, V. A. Sidorov¹, E. D. Bauer¹, N. N. Mel'nik³, N. J. Curro², J. D. Thompson² & S. M. Stishov¹

¹Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Moscow region, Russia
²Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
³Lebedev Physics Institute, Russian Academy of Sciences, 117924 Moscow, Russia

NATURE | VOL 428 | 1 APRIL 2004 | www.nature.com/nature
Bloch to Wannier Representation

\[ g(k, q) = \sum_{R_e, R_p} e^{i k \cdot R_e} e^{i q \cdot R_p} u_q U_{k+q} g(R_e, R_p) U_{k}^\dagger \]
\[ g(k, q) = \sum_{R_e, R_p} e^{i k \cdot R_e} e^{i q \cdot R_p} u_q U_{k+q} g(R_e, R_p) U_k^\dagger \]

Bloch

\[ \langle m0_e | \Delta_{\kappa\alpha, R_p} V(r) | nR_e \rangle \]

Wannier
Wannier Representation

\[ \langle m_0 e | \Delta_{\kappa \alpha, R_p} V(r) | n R_e \rangle \]
Electron Self-energy

\[ \Sigma = i \int \frac{d^2}{(2\pi)^4} |g(1, 2)|^2 D(1 - 2) G(2) \]

YIELDS A MASS ENHANCEMENT AND ASSOCIATED “KINK” AT THE FERMI SURFACE. “KINKS” HAVE BEEN OBSERVED IN ARPES DATA AND INTERPRETED AS SIGNATURES OF STRONG ELECTRON-PHONON COUPLING.
Electron-Phonon Interaction in the Photoemission Spectrum of La$_{2-x}$Sr$_x$CuO$_4$ from First Principles

“Kink” (for example, Lanzara et al, Nature) 2001

By measuring the change in slope, the electron-phonon coupling is estimated
CONCLUSION

BASED ON THE WANNIER FORMALISM FOR CALCULATING ELECTRON-PHONON SELF-ENERGIES, THE COUPLING IS 1/7 OF WHAT IS NEEDED TO REPRODUCE THE OBSERVED ARPES “KINKS”
EINSTEIN’S VIEW

Title of 1905 photoelectric effect paper:
"Concerning the generation and transformation of light from a heuristic point of view”

heuristic = model (an emergent view)
EMERGENCE

HENRI BERGSON (1859-1941)
“all we sense are images”
EINSTEIN’S VIEW

Title of 1905 photoelectric effect paper:
"Concerning the generation and transformation of light from a heuristic point of view"
heuristic = model (an emergent view)

\[ a(\text{reductionism}) + b(\text{emergence}) \]

WHERE BOTH \( a \) AND \( b \) WERE FUNCTIONS OF TIME
Standard Model =
“interacting atoms” model +
“elementary excitations” model
(reductionism + emergent behavior)
Standard Model = “interacting atoms” model + “elementary excitations” model
(reductionism + emergent behavior)

Theorists can explain and predict ground and excited state properties of many condensed matter systems, but experimentalists still make the decisions on “what’s right”. They also make the major new discoveries (for now).
HAPPY 50TH BIRTHDAY TO PHYSICAL REVIEW LETTERS AND MANY THANKS TO THE PEOPLE WHO HAVE MADE IT SUCH A SUCCESS!
END