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From Discovery to Innovation...

Atomistic tight binding theory of optical properties of quantum dots and nanocrystals

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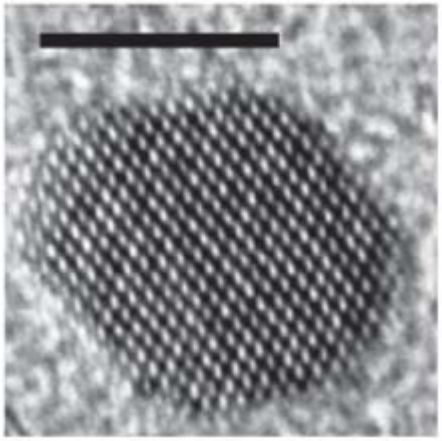
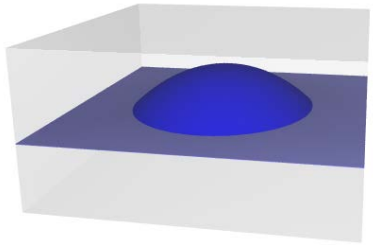
SEMICONDUCTOR NANOSTRUCTURES

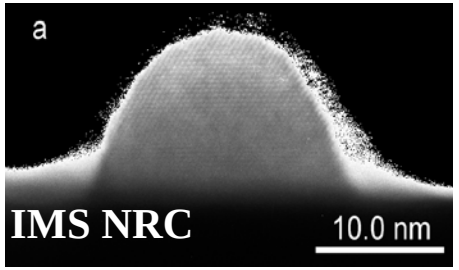
NANOCRYSTALS
~1000 ATOMS, ~10^4 ELE.



EFROS, EFIMOV

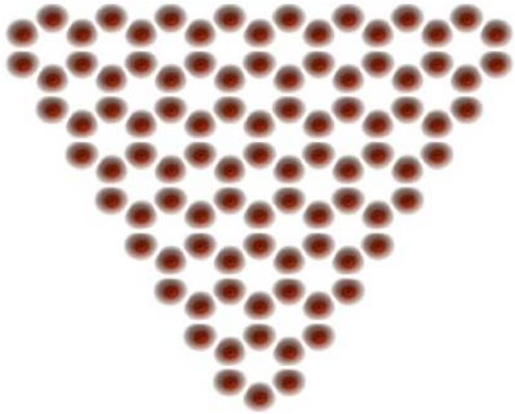
InAs/GaAs SELF-ASSEMBLED
QDOTS: 2 MLN ATOMS, ~10^7 ELE.



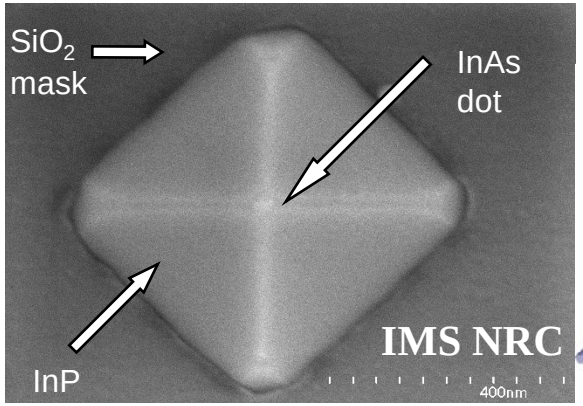


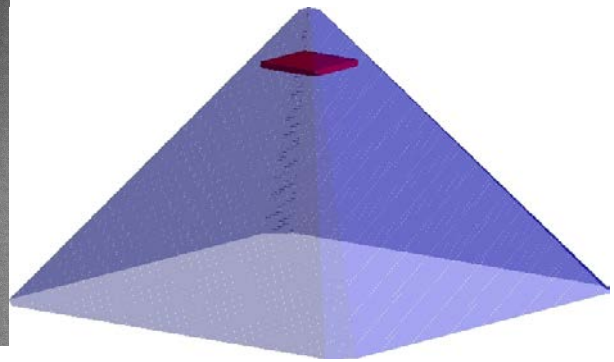
MANY GROUPS WORLDWIDE

GRAPHENE NANOISLANDS
500 ATOMS, ~10^3 ELE.



R. WILLIAMS, P. POOLE





InAs/InP QDOTS ON PATTERNED SUBSTRATES:
10 MLN ATOMS, ~10^8 ELE.

THEORETICAL TOOLS

1. **METHODS TREATING ALL ELECTRONS:**
   *** CONFIGURATION-INTERACTION: ~10 e, 2 ATOMS**
   *** DENSITY FUNCTIONAL THEORY: ~1000 e**

2. **ATOMISTIC QUASIPARTICLE APPROACHES:**
   CONDUCTION ELECTRON, VALENCE HOLE:
   *** EMPIRICAL PSEUDOPOTENTIAL – A. ZUNGER – 10^6 ATOMS**
   *** EBOM MODEL – Y.C. CHANG, MK, PH – 10^7 EFFECTIVE SITES**
   *** TIGHT BINDING –**
   KLIMECK, BRYANT, MK, MZ, PH – 10^7 ATOMS

3. **EFFECTIVE MASS APPROACHES:**
   *** K * P – 10^{24} ATOMS**
   *** SINGLE-BAND EMA – 10^{24} ATOMS**

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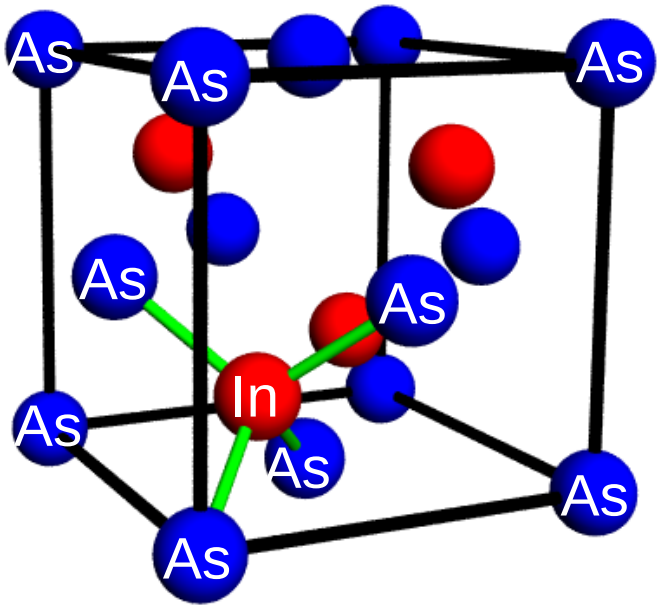
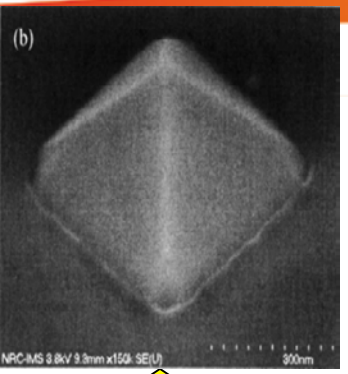
WHY ATOMISTIC MODELS?

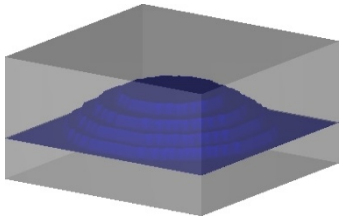


- **LACK OF INVERSION SYMMETRY OF THE LATTICE**
- **INTERFACES, INTERFACE ROUGHNESS**
- **STRAIN**
- **ATOMISTIC DISORDER**
- **RANDOM ALLOYING**
- **ELECTRON-HOLE EXCHANGE AND EXCITON FINE STRUCTURE**
- **IMPURITIES (ALSO MAGNETIC)**

COMPUTATIONAL PROCEDURE



model → **atomistic strain** → **Atomistic tight binding** → **MANY-BODY: CI** → **High Excitation PL**, **THz emission**, **Single photon gun**



Kinetic model: Shape, composition ~ 10^9 atoms

Mechanical ~ 10^9 atoms → Electronic ~10^6 atoms → Optical ~ 10 quasipaticles

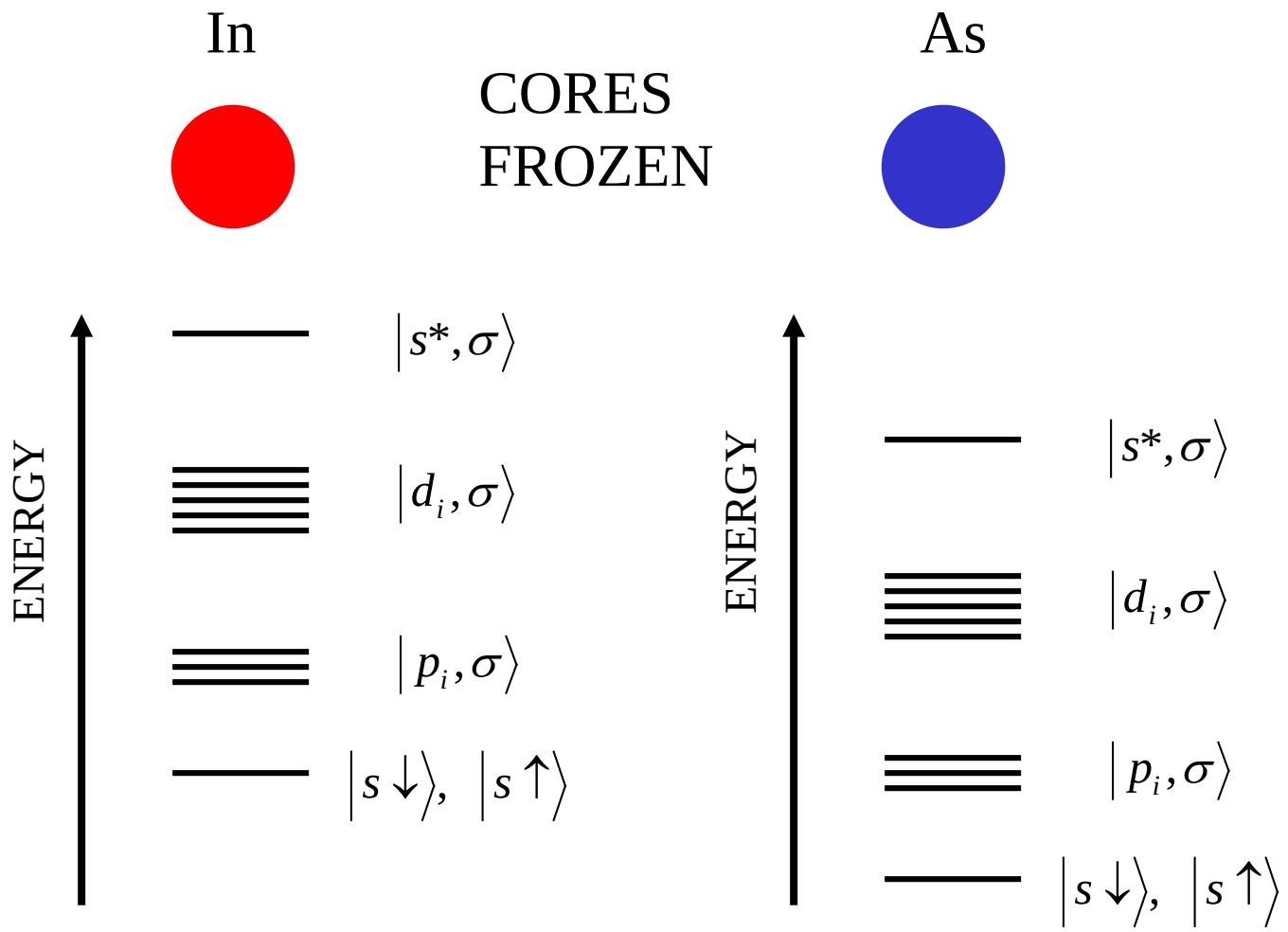
M.Zielinski,M.Korkusinski,P.Hawrylak,JAPL2009,PRB2009

TIGHT BINDING APPROACH
- FROM BULK TO NANOSTRUCTURE

(J. Slater and G. Koster, G. Klimeck, T. Boykin, G. Bryant,…….)

TIGHT BINDING APPROACH

(J. Slater and G. Koster, G. Klimeck, T. Boykin, G. Bryant)



BASIS ORBITALS
FOR THE VALENCE ELECTRON

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ORBITALS

ENERGY

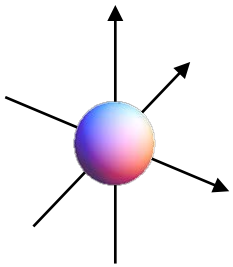
$|s^*,\sigma\rangle$

$|d_i,\sigma\rangle$

$|p_i,\sigma\rangle$

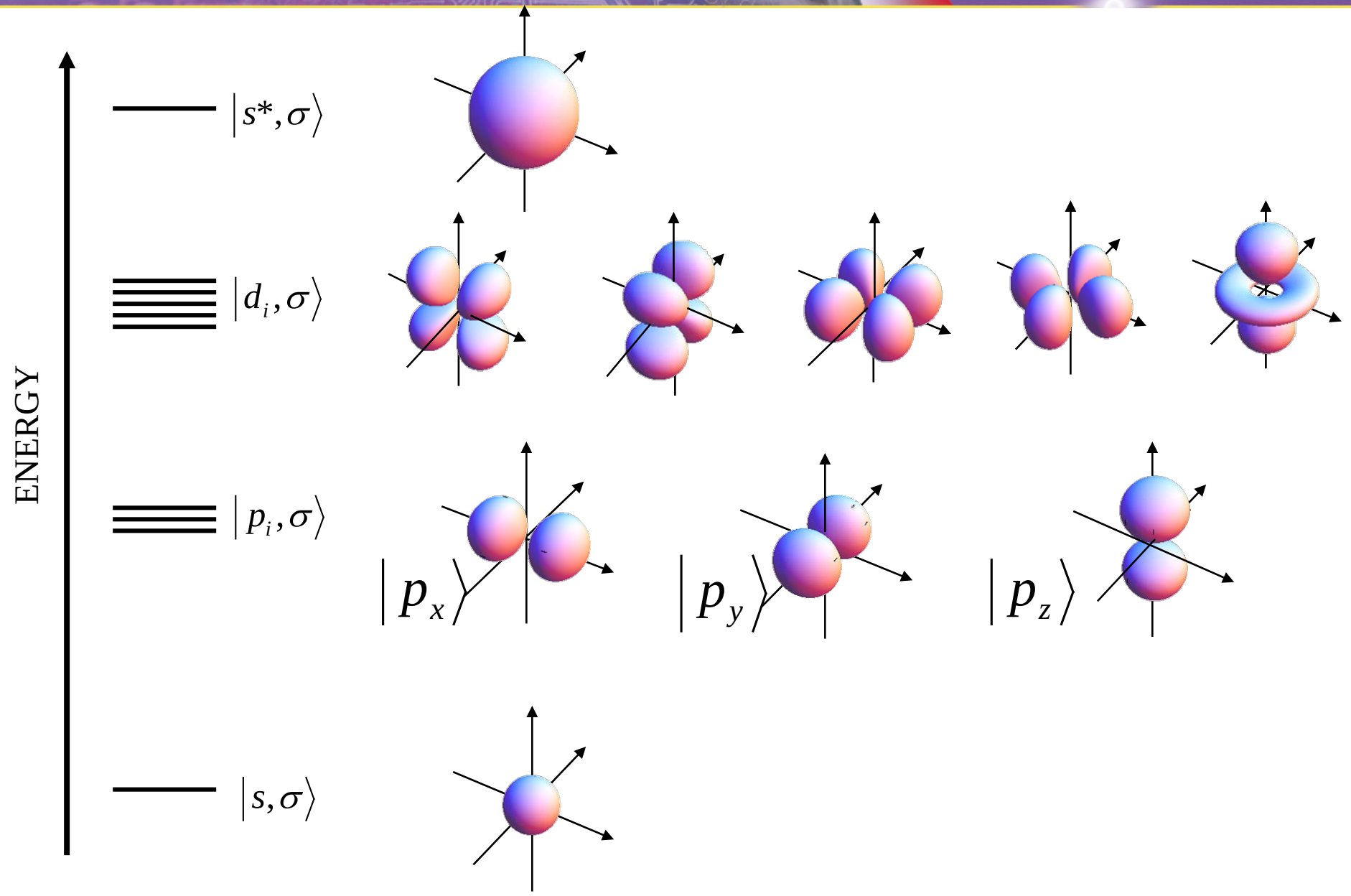
$|s,\sigma\rangle$

SLATER ORBITALS
A “HOLLOW SPHERE”

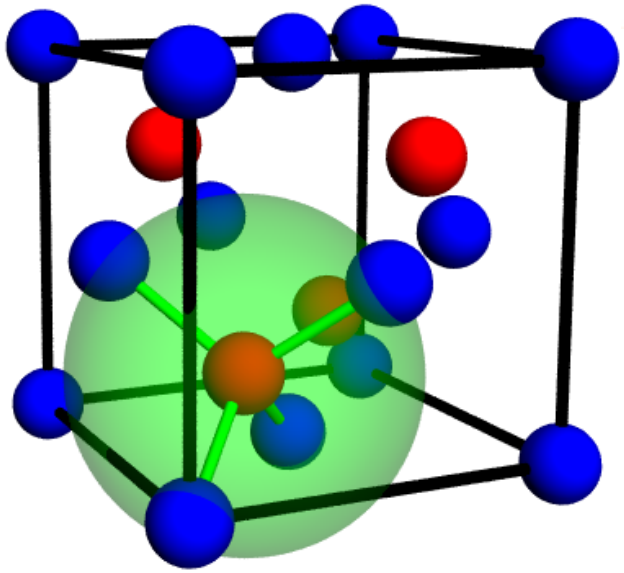


$$\langle r|s\rangle = N_{\alpha\beta} r^{\alpha} e^{-\beta r} Y_{00}(\theta,\varphi)$$

ORBITALS


ENERGY
$|s^*,\sigma\rangle$
$|d_i,\sigma\rangle$
$|p_i,\sigma\rangle$
$|p_x\rangle$
$|p_y\rangle$
$|p_z\rangle$
$|s,\sigma\rangle$

TIGHT-BINDING HAMILTONIAN



LCAO APPROACH

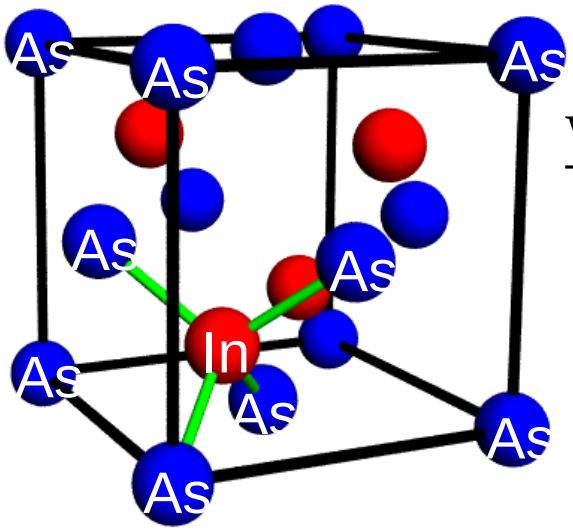
$$\varphi_l(r) = \sum_{R=1}^{N} \sum_{\alpha=1}^{20} \phi_{l,\alpha}(R) u_\alpha (r - R)$$

ATOMIC ORBITALS

R = ATOM INDEX

α = ORBITAL INDEX (INCLUDING SPIN)

TIGHT-BINDING HAMILTONIAN



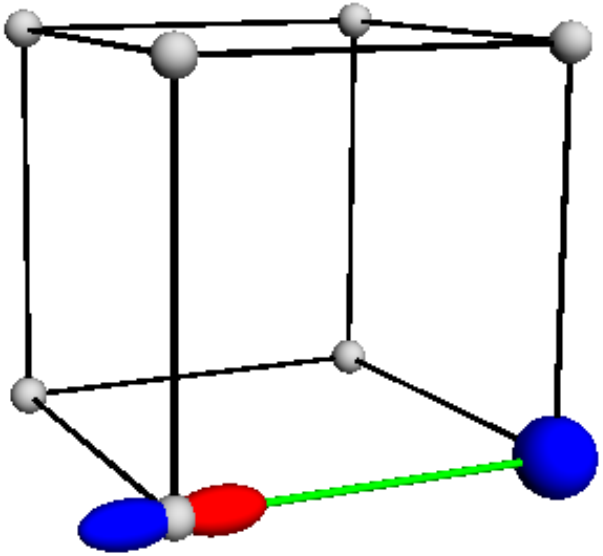
WE DO NOT COMPUTE THE ELEMENTS YET

TIGHT-BINDING PARAMETRIZATION WITH 1st NEAREST NEIGHBORS

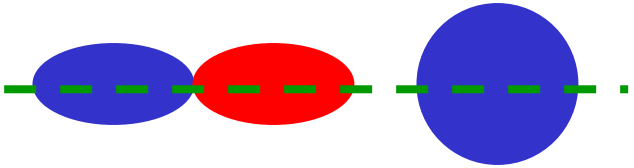
$$\hat{H} = \sum_{atoms\,R} \sum_{\substack{\alpha=1 \\ bands}}^{20} \varepsilon_{R\alpha} c^{+}_{R\alpha} c_{R\alpha} + \sum_{atoms\,R} \sum_{\substack{\alpha=1 \\ bands}}^{20} \sum_{\substack{\alpha'\neq\alpha \\ bands}}^{20} \lambda^{SO}_{R\alpha\alpha'} c^{+}_{R\alpha} c_{R\alpha'}$$

$$+ \sum_{atoms\,R} \sum_{atoms\,R'=1}^{4nn} \sum_{\substack{\alpha=1 \\ bands}}^{20} \sum_{\substack{\alpha'=1 \\ bands}}^{20} t_{R\alpha,R'\alpha'} c^{+}_{R\alpha} c_{R'\alpha'}$$

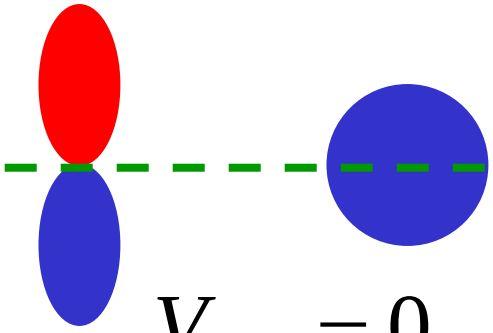
TIGHT-BINDING PARAMETERS



CASE OF SIMPLE CUBIC LATTICE



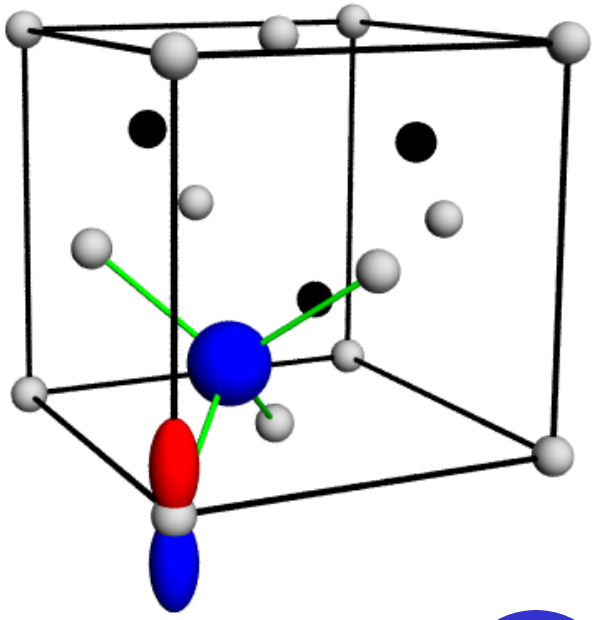
$$V_{sp\sigma} \neq 0$$

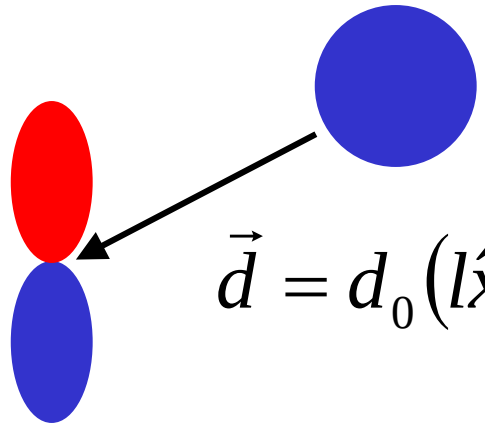


$$V_{sp\pi} = 0$$

TIGHT-BINDING PARAMETERS

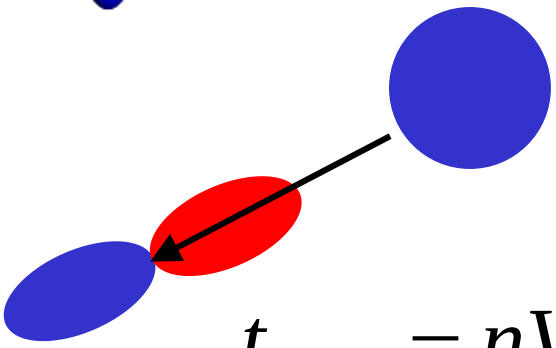
ZINCBLENDE LATTICE: TETRAHEDRAL COORDINATION



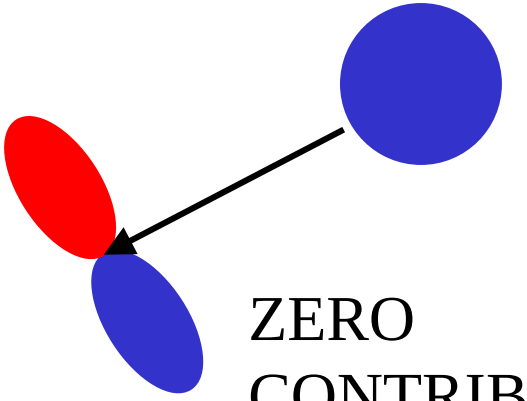


$$\vec{d} = d_0\left(l\hat{x} + m\hat{y} + n\hat{z}\right)$$

DECOMPOSE ORBITALS:



$$t_{sa,zc} = nV_{sa,pc\sigma}$$



ZERO CONTRIBUTION

TIGHT-BINDING PARAMETERS

SLATER-KOSTER RULES – EXPRESSIONS FOR ANY PAIR OF ORBITALS

TABLE I. Energy integrals for crystal in terms of two-center integrals.

$E_{s,s}$	$(ss\sigma)$
$E_{s,x}$	$l(sp\sigma)$
$E_{x,x}$	$l^2(pp\sigma)+(1-l^2)(pp\pi)$
$E_{x,y}$	$lm(pp\sigma)-lm(pp\pi)$
$E_{x,z}$	$ln(pp\sigma)-ln(pp\pi)$
$E_{s,xy}$	$\sqrt{3}lm(sd\sigma)$
E_{s,x^2-y^2}	$\frac{1}{2}\sqrt{3}(l^2-m^2)(sd\sigma)$
$E_{s,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)](sd\sigma)$
$E_{x,xy}$	$\sqrt{3}l^2m(pd\sigma)+m(1-2l^2)(pd\pi)$
$E_{x,yz}$	$\sqrt{3}lmn(pd\sigma)-2lmn(pd\pi)$
$E_{x,zx}$	$\sqrt{3}l^2n(pd\sigma)+n(1-2l^2)(pd\pi)$
E_{x,x^2-y^2}	$\frac{1}{2}\sqrt{3}l(l^2-m^2)(pd\sigma)+l(1-l^2+m^2)(pd\pi)$
E_{y,x^2-y^2}	$\frac{1}{2}\sqrt{3}m(l^2-m^2)(pd\sigma)-m(1+l^2-m^2)(pd\pi)$
E_{z,x^2-y^2}	$\frac{1}{2}\sqrt{3}n(l^2-m^2)(pd\sigma)-n(l^2-m^2)(pd\pi)$
$E_{x,3z^2-r^2}$	$l[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}ln^2(pd\pi)$
$E_{y,3z^2-r^2}$	$m[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)-\sqrt{3}mn^2(pd\pi)$
$E_{z,3z^2-r^2}$	$n[n^2-\frac{1}{2}(l^2+m^2)](pd\sigma)+\sqrt{3}n(l^2+m^2)(pd\pi)$
$E_{xy,xy}$	$3l^2m^2(dd\sigma)+(l^2+m^2-4l^2m^2)(dd\pi)+(n^2+l^2m^2)(dd\delta)$
$E_{xy,yz}$	$3lm^2n(dd\sigma)+ln(1-4m^2)(dd\pi)+ln(m^2-1)(dd\delta)$
$E_{xy,zx}$	$3l^2mn(dd\sigma)+mn(1-4l^2)(dd\pi)+mn(l^2-1)(dd\delta)$
E_{xy,x^2-y^2}	$\frac{3}{2}lm(l^2-m^2)(dd\sigma)+2lm(m^2-l^2)(dd\pi)+\frac{1}{2}lm(l^2-m^2)(dd\delta)$
E_{yz,x^2-y^2}	$\frac{3}{2}mn(l^2-m^2)(dd\sigma)-mn[1+2(l^2-m^2)](dd\pi)+mn[1+\frac{1}{2}(l^2-m^2)](dd\delta)$
E_{zx,x^2-y^2}	$\frac{3}{2}nl(l^2-m^2)(dd\sigma)+nl[1-2(l^2-m^2)](dd\pi)-nl[1-\frac{1}{2}(l^2-m^2)](dd\delta)$
$E_{xy,3z^2-r^2}$	$\sqrt{3}lm[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)-2\sqrt{3}lmn^2(dd\pi)+\frac{1}{2}\sqrt{3}lm(1+n^2)(dd\delta)$
$E_{yz,3z^2-r^2}$	$\sqrt{3}mn[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}mn(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}mn(l^2+m^2)(dd\delta)$
$E_{zx,3z^2-r^2}$	$\sqrt{3}ln[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}ln(l^2+m^2-n^2)(dd\pi)-\frac{1}{2}\sqrt{3}ln(l^2+m^2)(dd\delta)$
$E_{x^2-y^2,x^2-y^2}$	$\frac{3}{4}(l^2-m^2)^2(dd\sigma)+[l^2+m^2-(l^2-m^2)^2](dd\pi)+[n^2+\frac{1}{4}(l^2-m^2)^2](dd\delta)$
$E_{x^2-y^2,3z^2-r^2}$	$\frac{1}{2}\sqrt{3}(l^2-m^2)[n^2-\frac{1}{2}(l^2+m^2)](dd\sigma)+\sqrt{3}n^2(m^2-l^2)(dd\pi)+\frac{1}{4}\sqrt{3}(1+n^2)(l^2-m^2)(dd\delta)$
$E_{3z^2-r^2,3z^2-r^2}$	$[n^2-\frac{1}{2}(l^2+m^2)]^2(dd\sigma)+3n^2(l^2+m^2)(dd\pi)+\frac{3}{4}(l^2+m^2)^2(dd\delta)$

$$l^2(pp\sigma)+(1-l^2)(pp\pi)$$

100 RULES
REDUCE 100 HOPPING TERMS
TO 21 NONTRIVIAL PARAMETERS

J. SLATER & G. KOSTER, PHYS. REV. **94,** 1498 (1954)

TIGHT-BINDING HAMILTONIAN

$$
\mathbf{H}_{TB} = \begin{bmatrix}
\varepsilon^a_{S\downarrow} & 0 & 0 & 0 & 0 & & & & & \\
 & \varepsilon^a_{PX\downarrow} & i\Delta & 0 & 0 & & & & -\Delta & \\
 & & \varepsilon^a_{PY\downarrow} & 0 & 0 & & & & -i\Delta & \\
 & & & \varepsilon^a_{PZ\downarrow} & 0 & & \Delta & i\Delta & & \\
 & & & & \varepsilon^a_{S^*\downarrow} & & & & & \\
 & & & & & \varepsilon^a_{S\uparrow} & 0 & 0 & 0 & 0 \\
 & & & & & & \varepsilon^a_{PX\uparrow} & -i\Delta & 0 & 0 \\
 & & & & & & & \varepsilon^a_{PY\uparrow} & 0 & 0 \\
 & & & & & & & & \varepsilon^a_{PZ\uparrow} & 0 \\
 & & & & & & & & & \varepsilon^a_{S^*\uparrow}
\end{bmatrix}
$$

ANION

$$
\begin{bmatrix}
t_{SS} & t_{SPX} & t_{SPY} & t_{SPZ} & t_{SS^*} & & & & & \\
t_{PXS} & t_{PXPX} & t_{PXPY} & t_{PXPZ} & t_{PXS^*} & & & & & \\
t_{PYS} & t_{PYPX} & t_{PYPY} & t_{PYPZ} & t_{PYS^*} & & & & & \\
t_{PZS} & t_{PZPX} & t_{PZPY} & t_{PZPZ} & t_{PZS^*} & & & & & \\
t_{S^*S} & t_{S^*PX} & t_{S^*PY} & t_{S^*PZ} & t_{S^*S^*} & & & & & \\
 & & & & & t_{SS} & t_{SPX} & t_{SPY} & t_{SPZ} & t_{SS^*} \\
 & & & & & t_{PXS} & t_{PXPX} & t_{PXPY} & t_{PXPZ} & t_{PXS^*} \\
 & & & & & t_{PYS} & t_{PYPX} & t_{PYPY} & t_{PYPZ} & t_{PYS^*} \\
 & & & & & t_{PZS} & t_{PZPX} & t_{PZPY} & t_{PZPZ} & t_{PZS^*} \\
 & & & & & t_{S^*S} & t_{S^*PX} & t_{S^*PY} & t_{S^*PZ} & t_{S^*S^*}
\end{bmatrix}
$$

$$
\begin{bmatrix}
\varepsilon^c_{S\downarrow} & 0 & 0 & 0 & 0 & & & & & \\
 & \varepsilon^c_{PX\downarrow} & i\Delta & 0 & 0 & & & & -\Delta & \\
 & & \varepsilon^c_{PY\downarrow} & 0 & 0 & & & & -i\Delta & \\
 & & & \varepsilon^c_{PZ\downarrow} & 0 & & \Delta & i\Delta & & \\
 & & & & \varepsilon^c_{S^*\downarrow} & & & & & \\
 & & & & & \varepsilon^c_{S\uparrow} & 0 & 0 & 0 & 0 \\
 & & & & & & \varepsilon^c_{PX\uparrow} & -i\Delta & 0 & 0 \\
 & & & & & & & \varepsilon^c_{PY\uparrow} & 0 & 0 \\
 & & & & & & & & \varepsilon^c_{PZ\uparrow} & 0 \\
 & & & & & & & & & \varepsilon^c_{S^*\uparrow}
\end{bmatrix}
$$

CATION

$h.c.$

SPIN-ORBIT INTERACTION AFTER CHADI ET AL., PHYS. REV. B

TIGHT-BINDING PARAMETERS

TIGHT-BINDING PARAMETERS

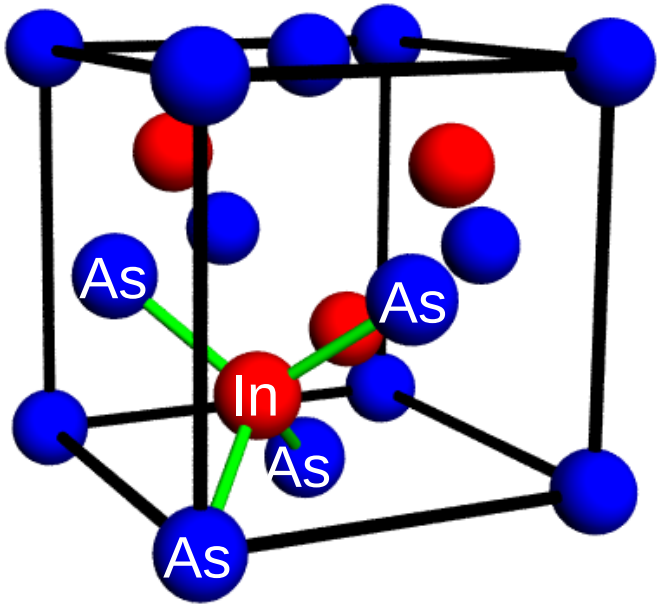
$$\hat{H} = \sum_{atoms\,R} \sum_{\substack{\alpha=1 \\ bands}}^{20} \varepsilon_{R\alpha} c^{+}_{R\alpha} c_{R\alpha} + \sum_{atoms\,R} \sum_{\substack{\alpha=1 \\ bands}}^{20} \sum_{\substack{\alpha' \neq \alpha \\ bands}}^{20} \lambda^{SO}_{R\alpha\alpha'} c^{+}_{R\alpha} c_{R\alpha'} + \sum_{atoms\,R} \sum_{atoms\,R'=1}^{4nn} \sum_{\substack{\alpha=1 \\ bands}}^{20} \sum_{\substack{\alpha'=1 \\ bands}}^{20} t_{R\alpha,R'\alpha'} c^{+}_{R\alpha} c_{R'\alpha'}$$

WE REQUIRE:

- 4 ONSITE ENERGIES FOR ANION (S, P, D, S* ORBITALS)
- 4 ONSITE ENERGIES FOR CATION
- 2 SPIN-ORBIT CONSTANTS (ONE - ANION, ONE - CATION)
- 21 HOPPING PARAMETERS

WE SET UP THE TB HAMILTONIAN FOR THE BULK AND FIT THE CHARACTERISTIC POINTS OF THE BRILLOUIN ZONE

TREATMENT OF BULK

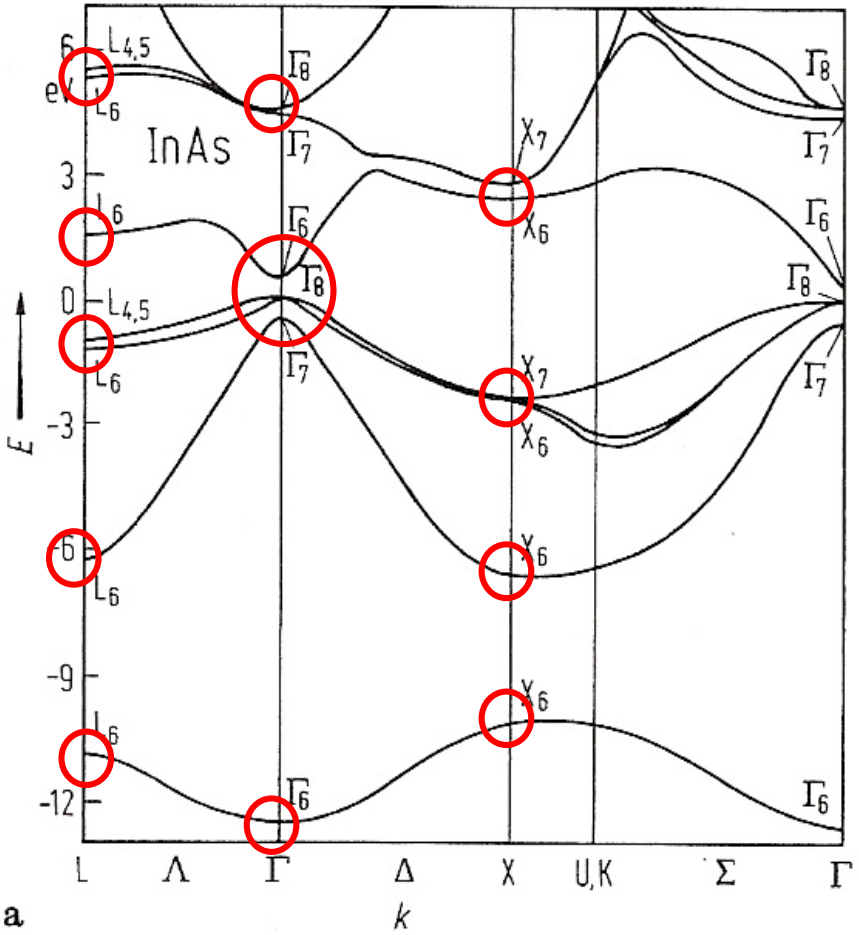


BASIS OF BLOCH SUMS

$$\left|\Psi_{ANION}\right\rangle = \sum_{\alpha=1}^{20} A_{\alpha}^{ANION} \left(\frac{1}{\sqrt{N}} \sum_{i,BLUE} e^{ikR_i} \varphi_{\alpha}\left(\vec{r} - \vec{R}_i\right) \right)$$

$$\left|\Psi_{CATION}\right\rangle = \sum_{\alpha=1}^{20} B_{\alpha}^{CATION} \left(\frac{1}{\sqrt{N}} \sum_{j,RED} e^{ikR_j} \varphi_{\alpha}\left(\vec{r} - \vec{R}_j\right) \right)$$

FITTING PROCEDURE



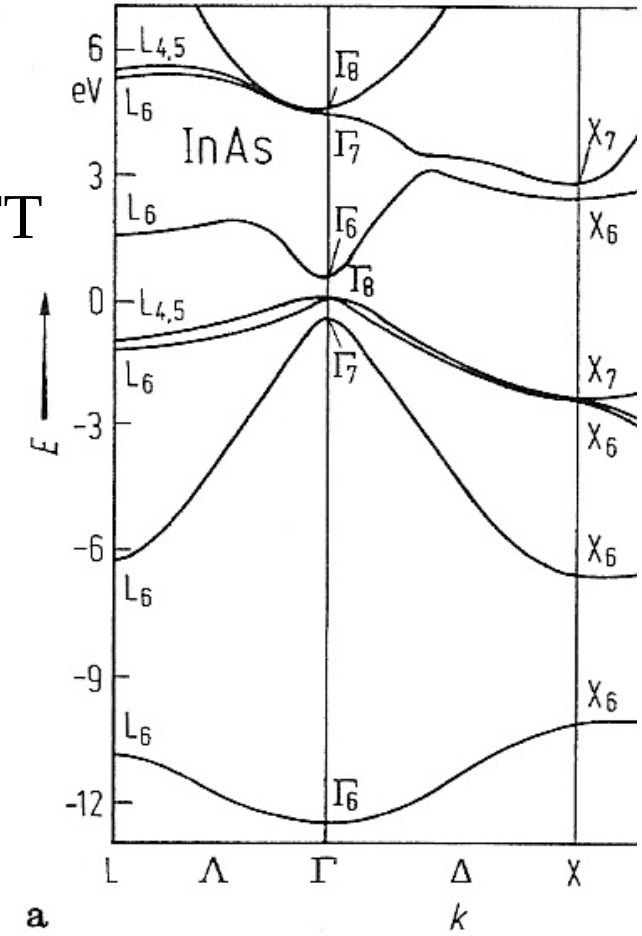
ENERGIES AND AVAILABLE EFFECTIVE MASSES FITTED USING GENETIC ALGORITHM

EXAMPLE: InAs

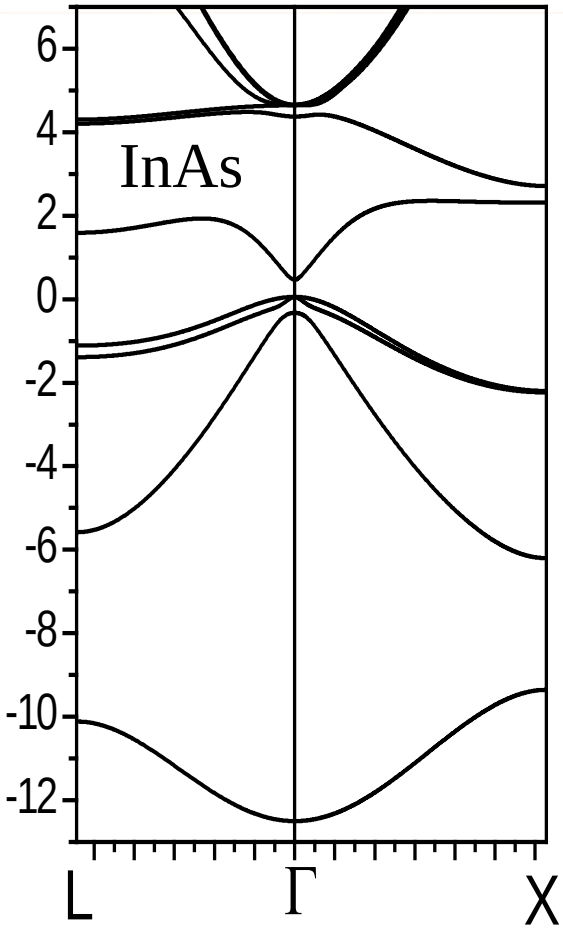
NONLOCAL PSEUDOPOTENTIAL, CHELIKOVSKY & COHEN, PRB

ELECTRONIC STRUCTURE CALCULATION
TIGHT BINDING BULK BANDSTRUCTURE

DFT



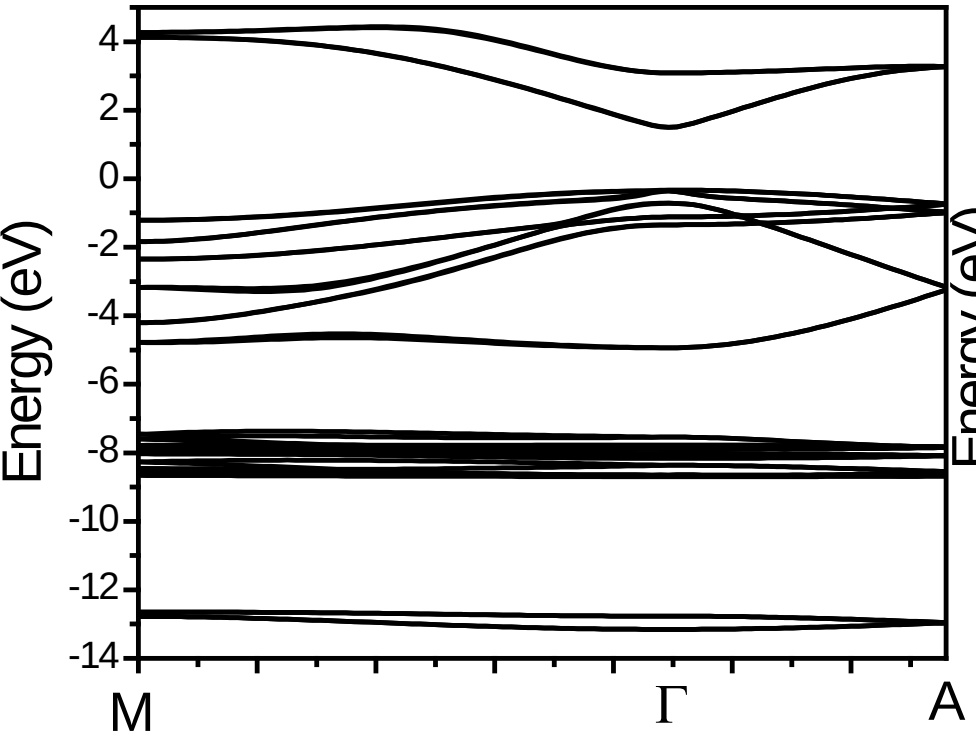
CHELIKOVSKY&COHEN

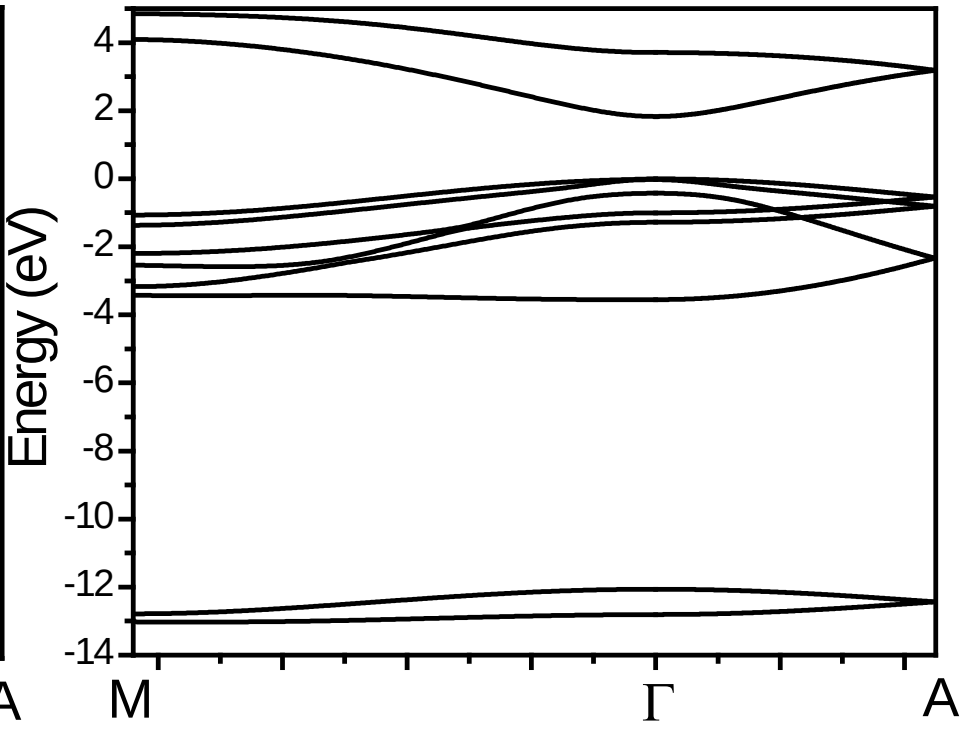


Tight binding

OUR FIT

BULK BAND STRUCTURE OF CdSe



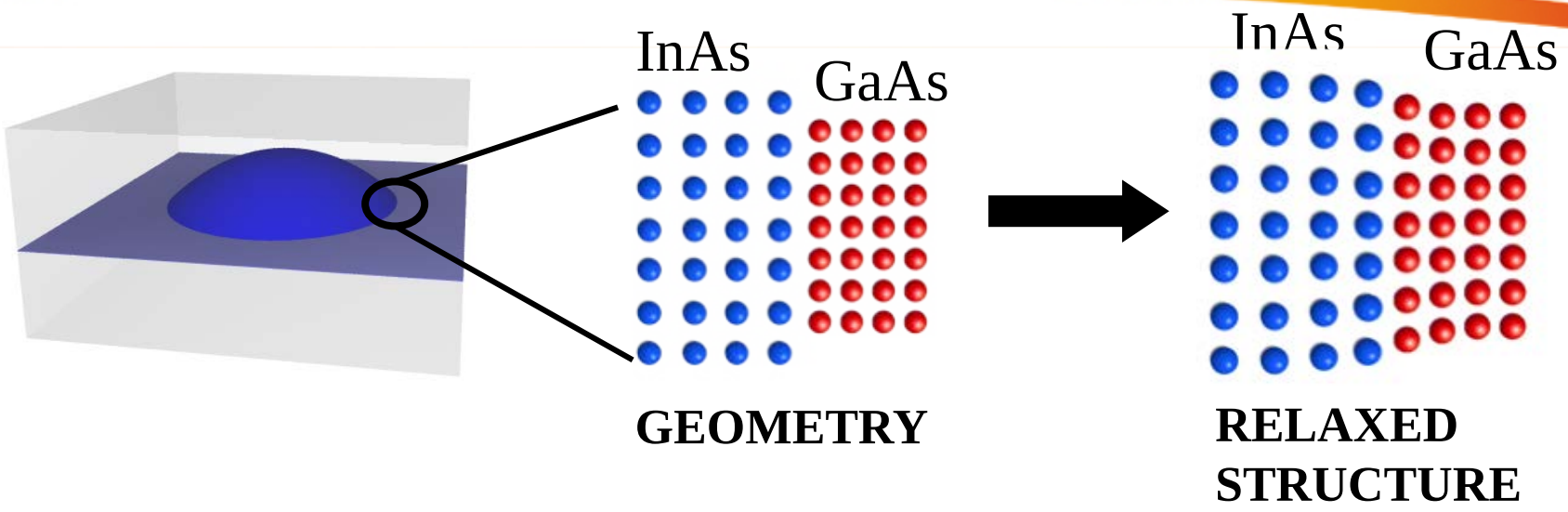


DFT + SCISSOR OPERATOR

OUR FIT

TREATMENT OF NANOSTRUCTURE

INTERFACES



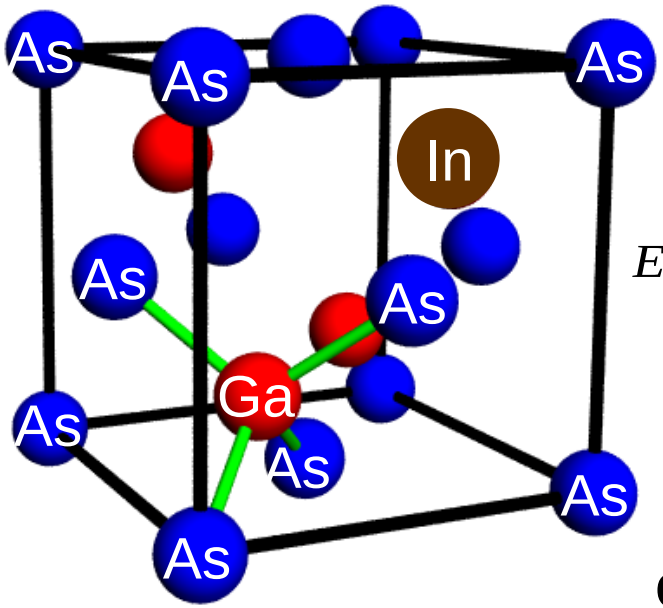
- **TB PARAMETERS ACROSS THE INTERFACE**
  - **INTERFACE PARAMETERS – NOT A PROBLEM FOR GaAs/InAs**
  - **BAND OFFSETS IN DIAGONAL MATRIX ELEMENTS**

- **CONSEQUENCES OF MODIFIED ATOMIC POSITIONS**

→ **STRAIN**

STRAIN

ATOMISTIC SIMULATION OF STRAIN



MINIMIZE TOTAL ELASTIC ENERGY

$$E_{TOT} = \frac{1}{2}\sum_{i}\sum_{j=1}^{4} A_{ij}\left(\left(\mathbf{R}_i - \mathbf{R}_j\right)^2 - \left(d_{ij}^0\right)^2\right)^2$$

$$+\sum_{i}\sum_{j=1}^{3}\sum_{k=j+1}^{4} B_{ijk}\left(\left(\mathbf{R}_j - \mathbf{R}_i\right)\left(\mathbf{R}_k - \mathbf{R}_i\right) - \cos\theta d_{ij}^0 d_{ik}^0\right)^2$$

OPTIMAL DISPLACEMENT FIELD FOUND WITH CONJUGATE-GRADIENT METHOD

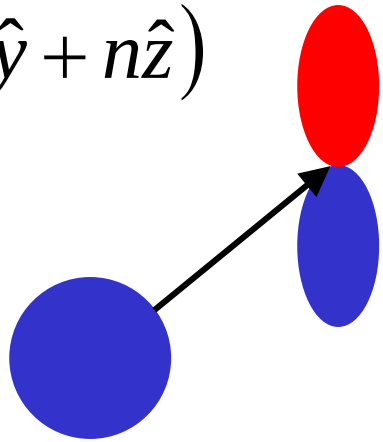
(P. Keating, A. Zunger, C. Pryor)

INCLUSION OF STRAIN

RESCALE MATRIX ELEMENTS BY DIRECTIONAL COSINES AND BOND STRETCHING TERMS (HARRISON'S LAW)

NO STRAIN

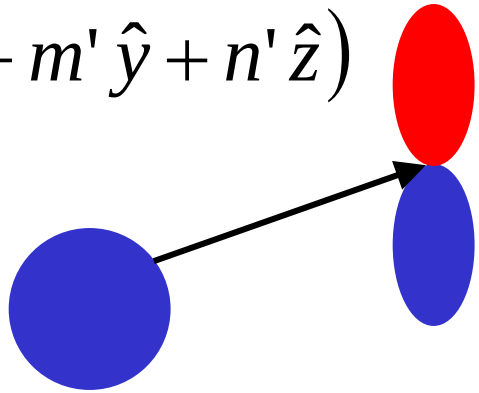
$$\vec{d} = d_0\left(l\hat{x} + m\hat{y} + n\hat{z}\right)$$



$$t_{sa,zc} = nV_{sa,pc\sigma}$$

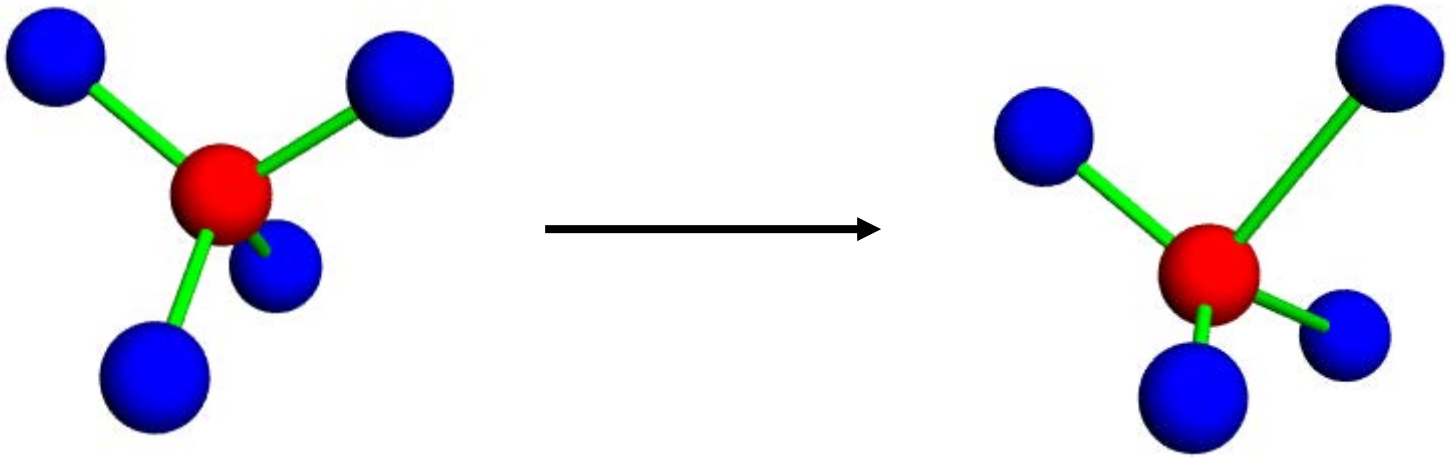
WITH STRAIN

$$\vec{d}' = d'\left(l'\hat{x} + m'\hat{y} + n'\hat{z}\right)$$



$$t'_{sa,zc} = n'V_{sa,pc\sigma}\left(\frac{d}{d_0}\right)^{\eta_{SPz}}$$

SHIFTS OF DIAGONAL TERMS



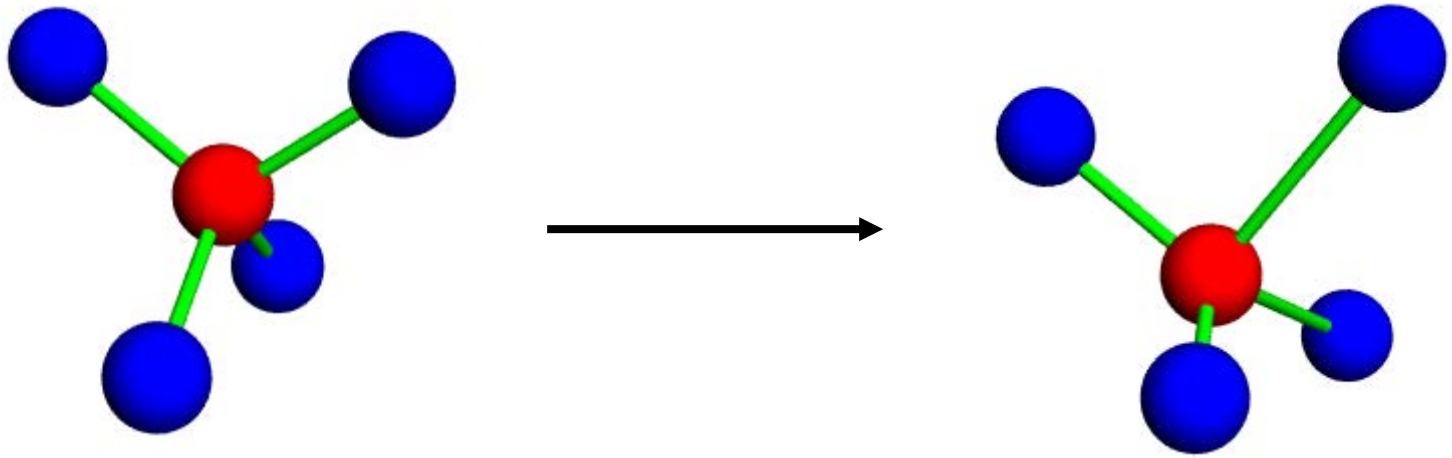
LOEWDIN-ORTHOGONALIZED BASIS:

$$\left|\Phi\right\rangle_i = \left|R,\alpha\right\rangle - \frac{1}{2}\sum_{R'\,\beta} S_{R\alpha,R'\,\beta}\left|R',\beta\right\rangle$$

S MATRIX CHANGES AS ATOMS ARE DISPLACED

T.B. BOYKIN, G. KLIMECK, PRB

SHIFTS OF DIAGONAL TERMS



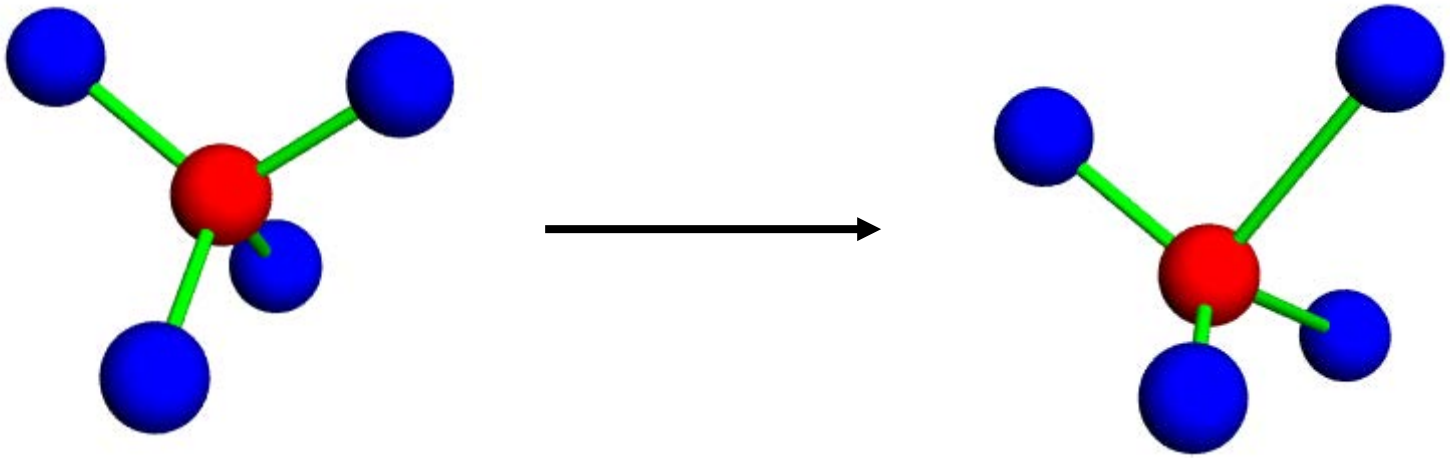
DIAGONAL HAMILTONIAN ELEMENTS

$$\varepsilon_{R\alpha} = {}_i\langle \Phi | H | \Phi \rangle_i \approx \langle R,\alpha | H | R,\alpha \rangle - \sum_{R'\beta} S_{R\alpha,R'\beta} \langle R,\alpha | H | R',\beta \rangle$$

SENSITIVE TO STRAIN!

T.B. BOYKIN, G. KLIMECK, PRB

SHIFTS OF DIAGONAL TERMS



PROCEDURE: USE EXTENDED HUECKEL RULE:

$$S_{R\alpha,R'\beta} \approx A\frac{t_{R\alpha,R'\beta}}{\varepsilon_{R\alpha}^{ATOM}+\varepsilon_{R'\beta}^{ATOM}}$$

"BARE" ATOMIC ENERGIES

$$\varepsilon_{\vec{R}\alpha}=\varepsilon_{\vec{R}\alpha}^{0}+\sum_{\vec{R}'\in nn}\sum_{\beta}C_{(\vec{R}\alpha,\vec{R}'\beta)}\frac{\left(t_{\vec{R}\alpha,\vec{R}'\beta}^{0}\right)^2-\left(t_{\vec{R}\alpha,\vec{R}'\beta}^{'}\right)^2}{\varepsilon_{\vec{R}\alpha}^{0}+\varepsilon_{\vec{R}'\beta}^{0}-\Delta E_{ATOM}}$$

C – PARAMETERS TO BE FITTED