# Poisson Boltzmann and the Double Helix

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# Nonlinearized DPBE

$$-\nabla \cdot (\epsilon(\mathbf{r})\nabla\Psi(\mathbf{r})) + \kappa^2(\mathbf{r})\sinh(\Psi(\mathbf{r})) = \left(\frac{4\pi e_c^2}{k_B T}\right)\sum_{i=1}^{N} z_i\delta(\mathbf{r} - \mathbf{r}_i).$$

- This is a three-dimensional second order nonlinear elliptic partial differential equation.

$$-\nabla \cdot (\bar{\mathbf{a}}(\mathbf{x})\nabla u(\mathbf{x})) + b(\mathbf{x}, u(\mathbf{x})) = f(\mathbf{x}) \text{ in } \Omega \subset \mathbb{R}^d,$$

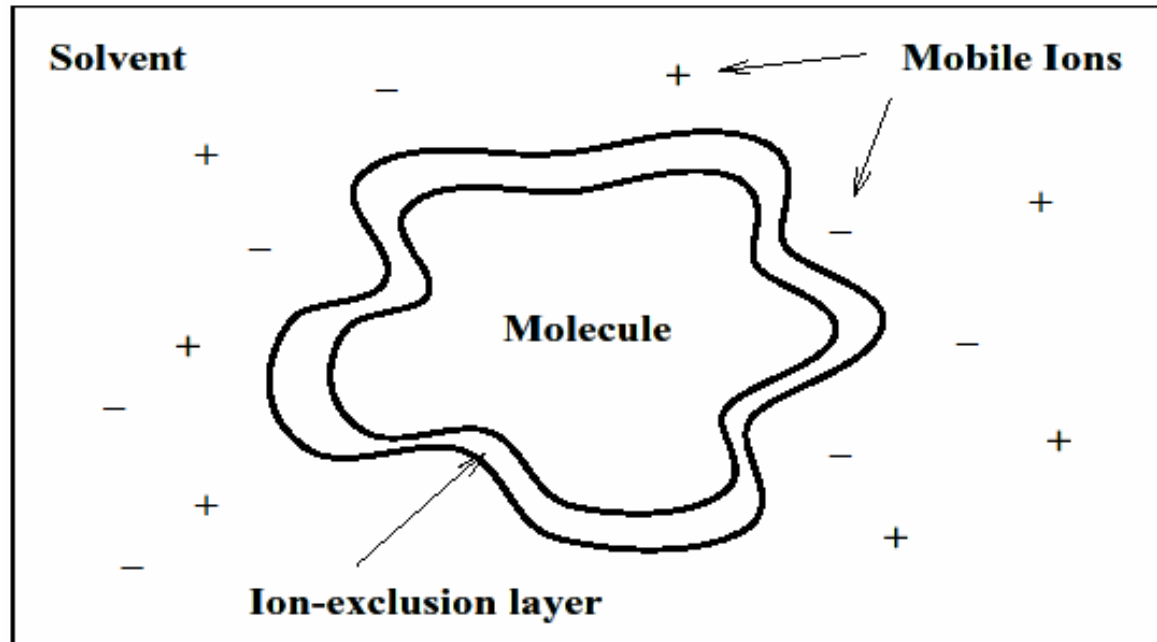- These nonlinear elliptic equations are of this general form; omega are regions of dielectric.

# Linearized PBE

$$-\nabla \cdot (\epsilon(\mathbf{r})\nabla u(\mathbf{r})) + \bar{\kappa}^2(\mathbf{r})u(\mathbf{r}) = \left(\frac{4\pi e_c^2}{k_B T}\right) \sum_{i=1}^{N_m} z_i \delta(\mathbf{r} - \mathbf{r}_i).$$

sinh is gone

$$\left( \quad -\nabla \cdot (\epsilon(\mathbf{r})\nabla \Psi(\mathbf{r})) + \kappa^2(\mathbf{r})\sinh(\Psi(\mathbf{r})) = \left(\frac{4\pi e_c^2}{k_B T}\right) \sum_{i=1}^{N} z_i \delta(\mathbf{r} - \mathbf{r}_i), \quad \right)$$

# Debye-Hückel model



The electrostatic potential satisfies Gauss' law in each of the three regions. In differential form this yields a separate Poisson equation

$$\nabla^2 \Phi_k(\mathbf{r}) = \frac{-4\pi \rho_k(\mathbf{r})}{\epsilon_k},$$

for each region $\Omega_k$, $k = 1, 2, 3$. In order to use these equations to determine the potential $\Phi_k(\mathbf{r})$ in each region, the charge density functions $\rho_k(\mathbf{r})$ must be defined.

# Delphi

- 1466 bio01a@wart ~/DelPhi/delphidata> ../delphi/delphi 1BPT.prm > 1BPT_log

```
1478 bio01a@wart ~/DelPhi/delphidata> cat 1BPT.prm
indi=2.
scale=1.8
perfil=80.
!bndcon=3
in(pdb,file="1BPT.pdb")
in(siz,file="default.siz")
in(crg,file="full.crg")
energy(c,s)
!out(phi,unit=14) ! don't want the potential map in the default file
out(modpdb,file="1BPT_delphi.pdb") ! use radii and charges
out(phi,file="1BPT_delphi.phi") ! output potential map
out(frc,file="1BPT_delphi.frc") ! field values to the .frc file
```

# Delphi 2

- 1467 bio01a@wart ~/DelPhi/delphidata> less full.crg
- atom__resnumbc_charge_
- nz    lys        1.0
- nh1   arg         0.5
- nh2   arg         0.5
- oe1   glu        -0.5
- oe2   glu        -0.5
- od1   asp        -0.5
- od2   asp        -0.5
- oxt          -1.00
- cu           2.0
- zn           2.0

# Current Work

- Beard and Schlick:
  - Developed the Discrete Surface Charge Optimization algorithm
  - Combines discrete surface charge assignment based on optimizing the Debye-Hückel approx. for electric field
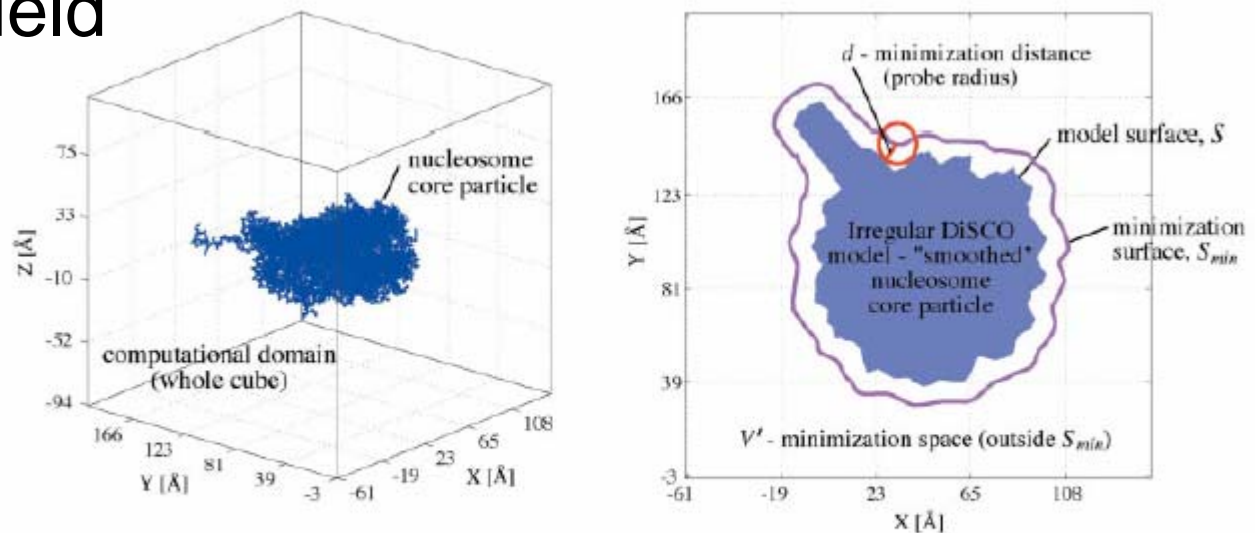


Figure 2. Left: the computational domain of the electrostatic potential and the electric field contains $65 \times 65 \times 65$ grid points enclosing the nucleosome core particle. Right: the minimization space $V'$ (of the residual) defines the computational domain separated from DiSCO surface by the minimization distance $d$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

# E Potential Refinement vs. E Field Refinement

## Results

### *Electrostatic Potential Refinement Versus Electric Field Refinement*

To compare the potential-based ($\phi$) refinement with the electric field-based (E) refinement, we use the original regular surface models[16] of the nucleosome core particle, as shown in Figure 1B. We define the resulting optimized charge sets as ($q_\phi$) and ($q_E$), respectively. The residual $R$ as a function of the salt concentration

$C_s$ is calculated for different numbers of discrete surface charges $N$, varying from 62 to 353, as shown at the top of Figure 4 based on both refinements.

From Figure 4 we see that the residual of E ($R_E$) is about twice as large as the residual of $\phi$ ($R_\phi$). This is reasonable given the relationship between E and $\phi$. Namely, when QNIFFT solves the nonlinear PBE using finite differences,[13] every grid point (except those on the boundary) is surrounded by six nearest grid points; because $E(r) = -\nabla\phi(r)$, one error of $\phi$ at one grid point causes

# If Emacs is the editor of the gods, where does Perl lie in the divine scheme?

```
# 31 - 38      Real(8.3)      x         Orthogonal coordinates for X in
#                                       Angstroms.
# 39 - 46      Real(8.3)      y         Orthogonal coordinates for Y in
#                                       Angstroms.
# 47 - 54      Real(8.3)      z         Orthogonal coordinates for Z in
#                                       Angstroms.
# 55 - 60      Real(6.2)      occupancy    Occupancy.
# 61 - 66      Real(6.2)      tempFactor   Temperature factor.
```

```
# A sample PDB line:
# ATOM     1  N   ARG     1      29.292  13.212 -12.751  1.00 33.78      1BPT 108
```

# Generate PDB files -- script with DelPhi

```perl
sub the_math($$@) {
    my ($phi,$dist,@atomdata) = @_;
    my (@rotatom, $x,$y,$z, $xp,$yp,$zp);
#   warn "the_math phi, dist $phi, $dist\n";
    $phi = $phi/360 * $M_PI;
    my $rcos = cos($phi);
    my $rsin = sin($phi);

    $x = $atomdata[0]; $y = $atomdata[1]; $z = $atomdata[2];
    # z axis rotation
    $xp = $x * $rcos - $y * $rsin;
    $yp = $x * $rsin + $y * $rcos;
    $zp = $z;

    # z axis translation
    $zp = $z + $dist;

    # fixed max 8 digits width, includes '.' and a trailing <sp>
    $xp = sprintf ("%6f", $xp); $yp = sprintf ("%6f", $yp); $zp = sprintf ("%6f", $zp);
    $xp = $xp." "; $yp = $yp." "; $zp = $zp." ";

    @rotatom = ( $xp,$yp,$zp );
}
```

# Calculate the total electrostatic grid energy

The two electrostatic intramolecular interactions are, (1) the potentials of the vacuum Coulomb interaction between all pairs of real and partial charges in the macromolecule, and (2) the charges with polarizable electrons in the molecule. The total electrostatic energy summing over all molecules is

$$\Delta G^{tt} = \sum_i \frac{q_i \phi_i}{2} = \sum_i \frac{q_i(\phi_i^{c} + \phi_i^{e} + \phi_i^{s} + \phi_i^{m})}{2},$$

where i is the potential experienced by a charge q_i, and {c, e, s, or m} represent Coulombic, electronic polarizability, solvent, and mobile ion interactions, respectively. This equation lacks terms for the solvation energy, that is, the interaction of a charge with its own induced polarization.