Modeling Confinement in Quantum Dot Solar Cells
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- Analytical solution vs. COMSOL simulation

Application and Validation of FEM for TISE

Particle in a box
Hydrogen atom

Efficient mesh

InAs/GaAs self-assembled QD

Substrate
Confining potential

COMOL
High quality pictures and data from several experiments

MATLAB
Run loops for lots of experiments to collect data and some pictures
The single-particle time-independent Schrödinger equation

\[ \hat{H}\psi(x, y, z) = E\psi(x, y, z) \]
\[ \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)\right]\psi(x, y, z) = E\psi(x, y, z) \]

In COMSOL Multiphysics

- Coefficient PDE form

\[ \lambda^2 e_a \psi - \lambda d_a \psi + \nabla \cdot (-c\nabla \psi - \alpha \psi + \gamma) + \beta \cdot \nabla \psi + \alpha \psi = f \quad \text{in} \, \Omega \]

with \( e_a = 0, d_a = 1, \alpha = 0, \gamma = 0, \beta = 0, f = 0 \), we get,

\[ \nabla \cdot (-c\nabla \psi) + a\psi = \lambda \psi \]

where \( c = \frac{\hbar^2}{2m_{\text{eff}}}, \lambda = E, a = V \)
• **Particle in a box**

• **Analytical solution**

• **One-dimensional box (infinite well)**

  Electron trapped, \( V=0 \) inside, \( V=\infty \) outside

  \[
  \left( -\frac{\hbar^2}{2m_e} \nabla^2 + 0 \right) \psi(x) = E\psi(x)
  \]

  \( \psi(x) = A \sin (kx) + B \cos (kx) \)

  \( \psi \) should be continuous \( \psi(x) = 0 \) at \( x = 0 \) and \( x = L \)

  \[
  \psi_n(x) = A \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, 4 \ldots
  \]

  Probability of finding the particle inside the box = 1

  \[
  \int_0^L \psi_n^2(x) \, dx = 1
  \]

  \[
  E_n = \frac{\hbar^2 \pi^2}{2m_e} \left( \frac{n^2}{L^2} \right)
  \]

  \[
  \psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}
  \]
• **Particle in a box**

• **Three-dimensional box**

\[
\left(-\frac{\hbar^2}{2m_e}\nabla^2 + 0\right)\psi_{n_xn_yn_z}(x, y, z) = E_{n_xn_yn_z}\psi_{n_xn_yn_z}(x, y, z)
\]

Similar to the case of one-dimensional

\[
E_{n_xn_yn_z} = \frac{\hbar^2 \pi^2}{2m_e} \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right]
\]

\[
\psi_{n_xn_yn_z}(x, y, z) = \left(\frac{2}{L}\right)^{\frac{3}{2}} \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}
\]

\[
n_x = 1, 2, 3, 4 \ldots; \quad n_y = 1, 2, 3, 4 \ldots; \quad n_z = 1, 2, 3, 4 \ldots
\]
• COMSOL simulation
  • Element (domain) type for 3D: tets, prisms...
  • Element order: linear, quadratic, cubic...
  • Element size parameters: $e_{\text{max}}, e_{\text{min}}, e_{\text{mgr}}, e_{\text{cf}}, e_{\text{ronr}}$
  • Optimization levels, Adaptive mesh refinement, elements’ quality

Cubic elements is better than quadratic elements

Mesh convergence study for an electron in a 3D box for ground state and first excited state
Mesh3, Mesh4 are more efficient and accurate. Mesh4 gives high quality elements.
Comparison of Relative errors $E_r$ of four mesh methods with respect to 14 distinct energy levels, all units of Relative errors are $10^{-5}$[eV]

<table>
<thead>
<tr>
<th>$(n_x, n_y, n_z)$</th>
<th>Deg.</th>
<th>$E_{\text{exact}}$</th>
<th>$E_{r, \text{mesh1}}$</th>
<th>$E_{r, \text{mesh2}}$</th>
<th>$E_{r, \text{mesh3}}$</th>
<th>$E_{r, \text{mesh4}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1,1,1)$</td>
<td>1</td>
<td>1.128090</td>
<td>0.266</td>
<td>0.800</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$(2,1,1), (1,2,1), (1,1,2)$</td>
<td>3</td>
<td>2.256180</td>
<td>1.06</td>
<td>3.06</td>
<td>0.0443</td>
<td>0</td>
</tr>
<tr>
<td>$(2,2,1), (2,1,2), (1,2,2)$</td>
<td>3</td>
<td>3.384270</td>
<td>2.33</td>
<td>7.12</td>
<td>0.0886</td>
<td>0.0590</td>
</tr>
<tr>
<td>$(3,1,1), (1,3,1), (1,1,3)$</td>
<td>3</td>
<td>4.136331</td>
<td>3.36</td>
<td>9.11</td>
<td>0.121</td>
<td>0.0484</td>
</tr>
<tr>
<td>$(2,2,2)$</td>
<td>1</td>
<td>4.512361</td>
<td>4.17</td>
<td>13.4</td>
<td>0.177</td>
<td>0.199</td>
</tr>
<tr>
<td>$(3,2,1), (3,1,2), (2,1,3), (2,3,1), (1,2,3), (1,3,2)$</td>
<td>6</td>
<td>5.264421</td>
<td>5.57</td>
<td>16.3</td>
<td>0.285</td>
<td>0.152</td>
</tr>
<tr>
<td>$(3,2,2), (2,3,2), (2,2,3)$</td>
<td>3</td>
<td>6.392511</td>
<td>8.35</td>
<td>26.2</td>
<td>0.532</td>
<td>0.125</td>
</tr>
<tr>
<td>$(4,1,1), (1,4,1), (1,1,4)$</td>
<td>3</td>
<td>6.768541</td>
<td>8.89</td>
<td>22.1</td>
<td>0.576</td>
<td>0.369</td>
</tr>
<tr>
<td>$(3,1,3), (3,3,1), (1,3,3)$</td>
<td>3</td>
<td>7.144571</td>
<td>10.2</td>
<td>29.1</td>
<td>0.728</td>
<td>0.391</td>
</tr>
<tr>
<td>$(4,2,1), (4,1,2), (1,4,2), (2,4,1), (1,2,4), (2,1,4)$</td>
<td>6</td>
<td>7.896631</td>
<td>12.3</td>
<td>34.5</td>
<td>0.975</td>
<td>0.557</td>
</tr>
<tr>
<td>$(3,3,2), (2,3,3), (3,2,3)$</td>
<td>3</td>
<td>8.272661</td>
<td>14.0</td>
<td>43.5</td>
<td>1.16</td>
<td>0.338</td>
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<tr>
<td>$(4,2,2), (2,4,2), (2,2,4)$</td>
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<td>9.024721</td>
<td>16.2</td>
<td>50.0</td>
<td>1.46</td>
<td>0.488</td>
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<tr>
<td>$(4,3,1), (4,1,3), (3,1,4), (3,4,1), (1,3,4), (1,4,3)$</td>
<td>6</td>
<td>9.776781</td>
<td>19.1</td>
<td>53.1</td>
<td>1.87</td>
<td>1.07</td>
</tr>
<tr>
<td>$(5,1,1), (1,5,1), (1,1,5), (1,3,3)$</td>
<td>4</td>
<td>10.15281</td>
<td>2.10</td>
<td>6.55</td>
<td>0.214</td>
<td>0.128</td>
</tr>
</tbody>
</table>

Mesh4: Accurate and efficient
Particle in a box

Ground state electron wavefunction for an electron in a 3D box

\[(1,1,1)\]

First excited electron wavefunction for an electron in a 3D box

\[(2,1,1),(1,2,1),(1,1,2)\]
• Particle in a box

n=3 to n=10 electron wave functions for an electron in a 3D box
Hydrogen atom

Analytical solution

\[ V_{\text{atom}} = -\frac{e^2}{4\pi\varepsilon_0 \sqrt{x^2 + y^2 + z^2}} \]

\[ \left( -\frac{\hbar^2}{2m_e} \nabla^2 + V \right) \psi(x, y, z) = E\psi(x, y, z) \]

\[ \psi(x, y, z) \rightarrow \psi(r, \theta, \varphi) \]

\[ x = r \sin \theta \cos \varphi \]
\[ y = r \sin \theta \sin \varphi \]
\[ z = r \cos \theta \]

\[ \frac{1}{r^2} \left( \frac{\partial}{\partial r} r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial \psi}{\partial \theta}) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \]

\[ + \frac{2m}{\hbar^2} (E + \frac{e^2}{4\pi\varepsilon_0 r})\psi = 0 \]

\[ E_n = -\frac{1}{n^2} \frac{m_e e^4}{8\varepsilon_0^2 \hbar^2} \]

\[ \psi(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m_l}(\theta, \varphi) \]

\[ \psi_{100}(r, \theta, \varphi) = R_{10}(r) Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} r e^{-\frac{r}{a_0}} \]

\[ \psi_{200}(r, \theta, \varphi) = R_{20}(r) Y_{00}(\theta, \varphi) = \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{3/2} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \]

\[ n = 1, 2, 3 \ldots \quad l = 0, 1, 2 \ldots (n - 1) \quad m_l = 0, \pm 1, \pm 2, \ldots, \pm l \]
- **Hydrogen atom**

- **Analytical solution**

\[
\begin{array}{|c|c|c|c|c|}
\hline
(n,l,m) & R_{nl} & Y_{lm}^m & \psi_{nlm} & E_{n_{exact}} \\
\hline
(1, 0, 0) & 2 \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} & \frac{1}{\sqrt{4\pi}} & \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} & -13.6062 \\
\hline
(2, 0, 0) & \frac{1}{2\sqrt{2}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} & \frac{1}{\sqrt{4\pi}} & \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} & -3.4015 \\
\hline
(2,1,0) & \frac{1}{2\sqrt{6}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \left( \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} & \frac{\sqrt{3}}{2\sqrt{\pi}} \cos(\theta) & \frac{1}{4\sqrt{2\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \left( \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \cos(\theta) & -3.4015 \\
\hline
(2, 1, \pm1) & \frac{1}{2\sqrt{6}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \left( \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} & \frac{\sqrt{3}}{2\sqrt{2\pi}} \sin(\theta) e^{\pm i\phi} & \frac{1}{8\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} \left( 2 - \frac{r}{a_0} \right) e^{-\frac{r}{2a_0}} \sin(\theta) e^{\pm i\phi} & -3.4015 \\
\hline
\end{array}
\]
- **Hydrogen atom**

- **COMSOL simulation**

- Shrink elements with a scale factor 0.05
- No. of quadratic elements is much greater than No. of cubic elements
- Denser mesh for the core of hydrogen atom where the electron wave functions are localized
Normalization of wave functions for the hydrogen atom, the figure shows the integral of $u^2$ modulus square for the entire domain equals 1. there are no probability for an electron to go outside of this domain
• Hydrogen atom

• Compared with two existing hydrogen electron orbitals
Ground state electron wavefunction of the hydrogen atom, quantum number: \((n, l, m) = (1,0,0)\), there is one 1s orbital.
First excited state electron wavefunction of the hydrogen atom, quantum number: \((n, l, m) = (2,0,0), (2,1,-1), (2,1,0), (2,1,1)\), there are one 2s orbital and three 2p orbitals.
By using isosurface function with 6 levels in COMSOL, we can get the shape of wave functions as well as the associated values of these 6 levels. First excited state electron wavefunction of the hydrogen atom, quantum number: \((n, l, m) = (2,0,0), (2,1,-1), (2,1,0), (2,1,1), (3,2,-2), (3,2,-1)\), there are one 3s orbital, three 3p orbitals and five 3d orbitals.
Cubic elements are better
Self-assembled quantum dot

\[ \nabla \cdot (-c \nabla \psi) + a \psi = \lambda \psi \text{ where } c = \frac{\hbar^2}{2m_{\text{eff}}} \text{, } \lambda = E \text{, } a = V \]

Dirichlet boundary condition

\[ m_{\text{InAs}} = 0.023m_e \]
\[ V_{\text{qld}} = 0 \]

\[ m_{\text{GaAs}} = 0.067m_e \]

\[ V_{\text{substrate1}} = 0.77 \]
\[ V_{\text{substrate2}} = V(z) = ((-1/800) \times z^2 + 0.77) \quad z \in [0, 20] \]
The confining potential energy in the substrate varies from $0.77 \text{[eV]}$ to a quadratic function of $z$: $(-1/800)*(z)^2+0.77)$ [eV], the Es, Ep shifts down 49.5[meV] and 110[meV], respectively
Conclusion

• Mesh convergence study (different order elements, particle in a box problem)

• Validate “particle in a box” and “hydrogen atom” problems by comparing with its analytical solutions and 3D models.

• Efficient mesh method (mesh the domains where the electron localized with cubic, high quality elements)

• The confining potential of the substrate plays an important role in engineering electron energies as well as wave functions in QDs
Thank you for your listening!

Questions?