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ONE DIMENSIONAL MODELS OF EXCITONS IN CARBON NANOTUBES

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Abstract. Excitons in carbon nanotubes may be modeled by two oppositely charged particles living on the surface of a cylinder. We derive three one dimensional effective Hamiltonians which become exact as the radius of the cylinder vanishes. Two of them are solvable.

1. Introduction and Motivation

An exciton in a straight carbon nanotube is reasonably well described by two oppositely charged spinless quantum particles living on the surface of an infinite cylinder $\mathcal{C}$. Once the center of mass has been removed and with "mathematical" units, the Hamiltonian governing such a system is

$$H := -\frac{\Delta}{2} - V^r, \quad V^r(x,y) := \frac{1}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}}$$

acting in $\mathcal{H} := L^2(\mathcal{C}, \mathbb{C})$. Here, $\mathcal{C}$ is the configuration space, i.e. $(rS^1) \times \mathbb{R}$, the infinite circular cylinder with radius r. x is the coordinate along the axis of $\mathcal{C}$ and y the length along transversal sections. Notice that V^r is just the Coulomb potential in the ambient space $\mathbb{R}^3$ expressed in the cylinder coordinates.

To present the content of this paper it is convenient to introduce the spectral decomposition of $-\frac{1}{2}\Delta_y := -\frac{1}{2}\partial_y^2$, i.e. the one dimensional Laplacian on $L^2(-\pi r, \pi r)$ with periodic boundary conditions:

$$-\frac{1}{2}\Delta_y = \bigoplus_{m=0}^{\infty} \frac{m^2}{2r^2} \Pi_m^r$$

where Π_m^r denotes the eigenprojector on the m^{th} eigenspace spanned by the transverse eigenmodes: $\chi_{\pm m}^r(y) := (2\pi)^{-\frac{1}{2}} e^{\pm imyr^{-1}}$. When the radius r gets smaller and smaller transitions between these transverse eigenmodes become more and more difficult since the spacing between the corresponding energies behaves like $\text{const}\, r^{-2}$. This is why when

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interested by the lowest energies of this system it is natural to consider the effective Hamiltonian obtained by projecting H on $\mathcal{H}_{\text{eff}} := \operatorname{Ran} \Pi_{\text{eff}} := \operatorname{Ran} 1 \otimes \Pi_0^r$, i.e. the span of χ_0^r. This effective Hamiltonian is unitarily equivalent to

$$H_{\text{eff}} := -\frac{1}{2}\Delta_x - V_{\text{eff}}^r, \quad V_{\text{eff}}^r(x) := \frac{1}{2\pi r}\int_{-\pi r}^{\pi r} \frac{dy}{\sqrt{x^2 + 4r^2 \sin^2 \frac{y}{2r}}}$$

acting in $L^2(\mathbb{R})$. It can be seen that V_{eff}^r has a $|x|^{-1}$ behaviour at infinity (see Eq. (2) below) and diverges logarithmically at the origin. This shows that V_{eff}^r is relatively bounded to H_0 with relative bound zero, so that H_{eff} is selfadjoint on the domain of $H_0 := -\frac{1}{2}\Delta_x$. Since H_{eff} does not seem to be analytically solvable, we propose two other one dimensional Hamiltonians, which are indeed solvable:
(1)

$$H_\delta := -\frac{1}{2}\Delta_x + \log(r^2)\delta(x) \quad (r < 1), \quad H_{\text{C}} := -\frac{1}{2}\Delta_x - \frac{1}{|x|} + \text{b.c. at } 0$$

both acting in $L^2(\mathbb{R})$; here δ denotes the Dirac distribution at 0, and b.c. means an appropriate boundary condition, see (9) for a precise definition.

These three effective Hamitonians are intrinsic since we are able to show, with H_{mod} denoting anyone of them, that: $\|(H-\zeta)^{-1} - (H_{\text{mod}} - \zeta)^{-1}\Pi_{\text{eff}}\|$ tends to 0 as $r \to 0$, for appropriate values of the spectral parameter ζ. Beside the fact that it shows the one dimensional character of excitons in carbon nanotubes, such a property is the starting point for perturbation theory and allows to compute the lowest part of spectrum of H, as well as the corresponding eigenstates, with rigorous error bounds.

As well known H_δ has a unique bound state with energy: $-2\log^2 r$; it follows at once that $E_0(r) := \inf H$ is a simple eigenvalue of H which fulfills

$$E_0(r) \overset{r \to 0}{=} -2\log^2 r(1 + o(1)).$$

That $E_0(r)$ tends to $-\infty$ as $r \to 0$ is an illustration of the binding enhancement of excitons in one dimensional structures, see [2] for a discussion of this phenomenon. With the Coulomb model H_{C} we have a much more accurate localization of $E_0(r)$ and we are in position to compute all negative excited states of H.

Most of the strategy and computations used here are borrowed from [1] where atoms in strong magnetic fields are studied, with however some discrepancies due to the fact that here we are dealing with a two dimensional problem instead of the three dimensional one for atoms. This is why in the rest of this paper we shall only sketch the proofs and stress the new aspects.

Finally let us mention two papers [3, 4] which deal with the same problem heuristically with variational methods.

2. Effective Hamiltonians

2.1. **Comparison of H_{eff} with the δ model.** V^r_{eff} has the following important scaling property:

$$V^r_{\text{eff}}(x) = \frac{1}{r} V^1_{\text{eff}}(\frac{x}{r}).$$

If V^1_{eff} would be in $L^1(\mathbb{R})$ this would imply by classical arguments that V^r_{eff} tends to δ as $r \to 0$. However V^1_{eff} is not in $L^1(\mathbb{R})$ as can be seen by expanding V^1_{eff} at infinity. First $V^1_{\text{eff}}(x) = 2\pi^{-1}|x|^{-1}K(-4x^{-2})$ where K denotes the complete elliptic integral of the first kind and then

$$V^1_{\text{eff}}(x) \overset{|x|\to\infty}{=} \frac{1}{|x|} + \mathcal{O}(|x|^{-3}). \tag{2}$$

Instead we shall prove in the next subsection that ($\log_2(x) := \log(\log(x))$)
(3)

$$\|(H_0+\alpha^2)^{-\frac{1}{2}}(V^r_{\text{eff}}+\log r^2\delta)(H_0+\alpha^2)^{-\frac{1}{2}}\| \overset{r\to 0}{=} \mathcal{O}\left(\frac{\log\alpha}{\alpha}\right) = \mathcal{O}\left(\frac{\log_2(r^{-1})}{\log(r^{-1})}\right)$$

with

$$\alpha = \sqrt{2}|\log r^2| \tag{4}$$

and $H_0 := -\frac{1}{2}\Delta_x$. Let $R_{\text{eff}}(\zeta) := (H_{\text{eff}} - \zeta)^{-1}$, $R_\delta(\zeta) := (H_\delta - \zeta)^{-1}$, then one has, using the symmetrized resolvent formula,

$$\|R_{\text{eff}}(\zeta) - R_\delta(\zeta)\| \le \|R_\delta(\zeta)\| \frac{\|K(\zeta)\|}{1 - \|K(\zeta)\|}$$

with $K(\zeta) := R_\delta(\zeta)^{\frac{1}{2}}(-V^r_{\text{eff}} - \log(r^2)\delta)|R_\delta(\zeta)|^{\frac{1}{2}}$. With the help of (3) one gets for r small enough

$$\begin{aligned} \|K(\zeta)\| &\le \|R_\delta(\zeta)^{\frac{1}{2}}(H_0+\alpha^2)^{\frac{1}{2}}\|^2 \,\text{const}\frac{\log\alpha}{\alpha} \\ &\le \|R_\delta(\zeta)^{\frac{1}{2}}(H_\delta+\alpha^2)^{\frac{1}{2}}\|^2 \|R_\delta(-\alpha^2)^{\frac{1}{2}}(H_0+\alpha^2)^{\frac{1}{2}}\|^2 \,\text{const}\frac{\log\alpha}{\alpha}. \end{aligned}$$

We assume now that

$$d_\delta(\zeta) := \text{dist}\,(\zeta, \text{spect}\, H_\delta) \ge c_\delta\alpha^2 \quad \text{with} \quad 0 < c_\delta \le 1, \tag{5}$$

then by spectral theorem $\|R_\delta(\zeta)^{\frac{1}{2}}(H_\delta+\alpha^2)^{\frac{1}{2}}\|^2 \le \max\{\alpha^2/d_\delta(\zeta), 1\} = 1/c_\delta$ and using Krein's formula, $\|R_\delta(-\alpha^2)^{\frac{1}{2}}(H_0+\alpha^2)^{\frac{1}{2}}\|^2 = 2$. At last we have obtained that under (5) and for r small enough

$$\|K(\zeta)\| \le \frac{2\text{const}}{c_\delta}\frac{\log\alpha}{\alpha}$$

so that $\|K(\zeta)\| \le \frac{1}{2}$, again for r small enough. Thus we have proven

Theorem 1. *Let* $\alpha := \sqrt{2}|\log r^2|$. *For any* $0 < c_\delta \leq 1$ *there exists* $r_\delta > 0$ *such that if* $d_\delta(\zeta) \geq c_\delta \alpha^2$ *and* $r < r_\delta$ *one has* $\zeta \in \rho(H_{\text{eff}})$, *the resolvent set of* H_{eff}, *and*

$$\|(H_{\text{eff}} - \zeta)^{-1} - (H_\delta - \zeta)^{-1}\| \leq \frac{C_\delta}{c_\delta} \frac{\log \alpha}{\alpha} \frac{1}{d_\delta(\zeta)}.$$

Here C_δ *is a constant which depends only on* V^1_{eff}.

By standard perturbation theory one gets:

Corollary. *In particular* $E_{\text{eff}}(r) := \inf H_{\text{eff}}$ *is a simple isolated eigenvalue of* H_{eff}. *Denote by* φ_{eff} *the corresponding eigenstate, and* φ_δ *the one of* H_δ, *then*

$$E_{\text{eff}}(r) \overset{r\to 0}{=} -2\log^2 r + \mathcal{O}\big(\log r^{-1} \log_2 r^{-1}\big)\,,$$

$$\|\varphi_{\text{eff}} - \varphi_\delta\| \overset{r\to 0}{=} \mathcal{O}\left(\frac{\log_2(r^{-1})}{\log r^{-1}}\right).$$

2.2. **Comparison of H_{eff} with the Coulomb model.** We start by showing various properties and approximations of V^r_{eff}. It is straightforward to compute $\hat{V}^1_{\text{eff}}$ explicitly: $\hat{V}^1_{\text{eff}}(p) = \sqrt{2}\pi^{-\frac{1}{2}}\, I_0(|p|)K_0(|p|)$, where I_0 and K_0 denote the modified Bessel functions of first and second kind respectively. From which follows at once that (γ denotes the Euler constant):

$$\sqrt{2\pi}\hat{V}^1_{\text{eff}}(p) \overset{p\to 0}{=} -2\log(|p|) + 2\,(-\gamma + \log 2) + \mathcal{O}(p^2 \log|p|) \tag{6}$$

and $\sqrt{2\pi}\hat{V}^1_{\text{eff}}(p) \overset{|p|\to\infty}{=} |p|^{-1} + \mathcal{O}(|p|^{-3})$. Thus we may assume that there exists $C_{\text{eff}} > 0$ so that $|\hat{V}^1_{\text{eff}}(p)|^2 \leq C^2_{\text{eff}}(\log^2|p| + 1)$. Let HS stand for Hilbert-Schmidt norm then

$$\|(H_0 + \alpha^2)^{-\frac{1}{2}} \hat{V}^r_{\text{eff}} (H_0 + \alpha^2)^{-\frac{1}{2}}\|^2_{\text{HS}} = \frac{1}{2\pi} \int_{\mathbb{R}\times\mathbb{R}} \frac{|\hat{V}^r_{\text{eff}}(p-q)|^2 dp dq}{(\frac{p^2}{2} + \alpha^2)(\frac{q^2}{2} + \alpha^2)}$$

$$\leq \frac{\sqrt{2}}{\pi\alpha} \int_{\mathbb{R}} \frac{|\hat{V}^1_{\text{eff}}(pr)|^2 dp}{p^2 + 8\alpha^2} \leq \frac{\sqrt{2}C^2_{\text{eff}}}{\pi\alpha} \int_{\mathbb{R}} \frac{(\log^2|pr| + 1)dp}{p^2 + 8\alpha^2}$$

$$\overset{(7)}{=} C^2_{\text{eff}} \frac{4 + \pi^2 + 9\log^2 2 + 4\log(r\alpha)\log(8r\alpha)}{8\alpha^2}.$$

This shows several properties: (a) V^r_{eff} is H_0-compact for any $r > 0$, (b) it follows that the essential spectrum of H_{eff} is $\mathbb{R}_+$. (c) Since it can be seen that the above bound may be made smaller than one if r is small enough and $0 < \alpha \leq \sqrt{2}|\log r^2|$, the number $-2\log^2 r^2$ is a lower bound on the spectrum of H_{eff} for such r's.

Again with (6) we get

$$\sqrt{2\pi}\hat{V}^r_{\text{eff}}(p) + \log r^2 \overset{p\to 0}{=} -2\log|p| + \mathcal{O}(1)$$

where the $\mathcal{O}(1)$ is valid on $]0, r^{-1}]$. Thus

$$\frac{\sqrt{2}}{\pi\alpha}\int_{|p|<r^{-1}} \frac{\left|\hat{V}^r_{\rm eff}(p) + \log r^2 \frac{1}{\sqrt{2\pi}}\right|^2 dp}{p^2+8\alpha^2} \le \frac{\rm const}{\alpha}\int_0^{r^{-1}} \frac{(\log^2 p + 1)dp}{p^2+8\alpha^2} = \mathcal{O}(\frac{\log^2\alpha}{\alpha^2}).$$

On the other hand:

$$\frac{\sqrt{2}}{\pi\alpha}\int_{|p|>r^{-1}} \frac{\left|\hat{V}^r_{\rm eff}(p) + \log r^2 \frac{1}{\sqrt{2\pi}}\right|^2 dp}{p^2+8\alpha^2} \le \frac{\rm const}{\alpha}\int_{r^{-1}}^{\infty} \frac{(\log^2(pr) + 1)dp}{p^2} = \mathcal{O}(\frac{r}{\alpha}).$$

Putting together the last two estimates proves (3).

Finally let $\sqrt{2\pi}\hat{V}^r_{\rm C}(p) := -2\log|pr| + 2(\log 2 - \gamma)$ then in view of (6) it follows that $p^{-1}\hat{X}^r := p^{-1}(\hat{V}^r_{\rm eff} - \hat{V}^r_{\rm C}) \in L^2(\mathbb{R})$; therefore

$$\|(H_0+\alpha^2)^{-\frac{1}{2}}(V^r_{\rm eff} - V^r_{\rm C})(H_0+\alpha^2)^{-\frac{1}{2}}\|^2_{\rm HS} \le \frac{\sqrt{2}}{\pi\alpha}\int_{\mathbb{R}} \frac{|\hat{X}^1(pr)|^2 dp}{p^2+8\alpha^2}$$

$$(8) = \frac{\sqrt{2}r}{\pi\alpha}\int_{\mathbb{R}} \frac{|\hat{X}^1(p)|^2 dp}{p^2+8r^2\alpha^2} \le \frac{\sqrt{2}r}{\pi\alpha}\int_{\mathbb{R}} \frac{|\hat{X}^1(p)|^2 dp}{p^2} = \mathcal{O}\left(\frac{r}{\alpha}\right).$$

Taking the inverse Fourier image of the distribution $-2\log|pr| + 2(\log 2 - \gamma)$ shows that

$$V_{\rm C}(x) = -\log\frac{r^2}{4}\delta(x) + {\rm fp}\frac{1}{|x|} \tag{9}$$

where ${\rm fp}\frac{1}{|x|}$ denotes the finite part of $|x|^{-1}$ distribution.

Combining (7) and (8) one sees that $V_{\rm C}$ is H_0-compact for any $r > 0$ so that $H_{\rm C} = H_0 - V_{\rm C}$ makes sense as a self adjoint operator with form domain $\mathcal{H}^1(\mathbb{R})$, the first Sobolev space. This shows also that the essential spectrum of $H_{\rm C}$ is $\mathbb{R}_+$. Since $H_{\rm C}$ commutes with the parity operator, its discrete spectrum may be decomposed in its odd and even part. By standard arguments, they both consist of simple eigenvalues and they intertwine. Looking at (9) one realizes that the odd spectrum does not depend on r and coincides with the spectrum of the Hydrogen atom in the s-wave sector:

$$\text{spect}_{\rm dis} H^{\rm odd}_{\rm C} = \{-\frac{1}{2}, -\frac{1}{8}, \ldots, -\frac{1}{2n^2}, \ldots\}.$$

Again looking at (9) one sees that the discrete even spectrum is monotone increasing as a function of r and that as r tends to 0 or ∞ the value of the corresponding eigenfunctions at the origin must tend to zero; in other words the discrete even spectrum converges to the odd one, except for the lowest eigenvalue which tends to $-\infty$ as r tends to 0. Finally we may estimate $\|(H_{\rm eff} - \zeta)^{-1} - (H_{\rm C} - \zeta)^{-1}\|$ as in the previous subsection with the help of (8).

Theorem 2. *Let* $\alpha := \sqrt{2}|\log r^2|$. *There exists* $C_{\rm C}$ *and* $r_{\rm C} > 0$ *such that if* $\alpha \geq d_{\rm C}(\zeta) := \mathrm{dist}\,(\zeta, \mathrm{spect}\, H_{\rm C}) \geq 2C_{\rm C} r\alpha$ *and* $0 < r < r_C$ *then*

$$\zeta \in \rho(H_{\rm eff}) \quad \text{and} \quad \|(H_{\rm eff} - \zeta)^{-1} - (H_{\rm C} - \zeta)^{-1}\| \leq C_{\rm C} \frac{r\alpha}{d_{\rm C}(\zeta)^2}.$$

For any eigenvalue $E_{\rm C}$ *with eigenvector* $\varphi_{\rm C}$ *of* $H_{\rm C}$ *there exist an eigenvalue* $E_{\rm eff}$ *of* $H_{\rm eff}$ *and an associated eigenvector* $\varphi_{\rm eff}$ *such that*

$$E_{\rm eff} - E_{\rm C} \overset{r \to 0}{=} \mathcal{O}(r\alpha), \quad \text{and} \quad \|\varphi_{\rm eff} - \varphi_{\rm C}\| \overset{r \to 0}{=} \mathcal{O}(r\alpha).$$

Moreover this exhausts the negative discrete spectrum of $H_{\rm eff}$.

2.3. **Reduction of H to $H_{\rm eff}$.** To compare H and $H_{\rm eff}$ we resort to the Feshbach reduction:

$$(H - \zeta)^{-1} = \begin{pmatrix} S & SV^r R \\ RV^r S & R + RV^r SV^r R \end{pmatrix}$$

with

$$\begin{cases} S := (H_{\rm eff} + W - \zeta)^{-1} \\ W := -\Pi_{\rm eff} V^r R V^r \Pi_{\rm eff} \\ R := (\Pi_{\rm eff}^{\perp} H \Pi_{\rm eff}^{\perp} - \zeta)^{-1}. \end{cases}$$

Here $\Pi_{\rm eff}^{\perp}$ projects on the orthogonal complement $\mathcal{H}_{\rm eff}$. The proof of the next theorem while classic is too involved technically to be reported in this short article. It follows closely [1] except for the estimate

$$\|(H_0 + \beta)^{-\frac{1}{2}} W (H_0 + \beta)^{-\frac{1}{2}}\| \leq \frac{\pi^2}{3\sqrt{2}} \|V_{\rm eff}^1\|_2^2 \frac{r}{\beta},$$

which cannot rely on Hardy's inequality since here V^r has a Coulomb singularity in dimension two and not three. We denote by $\mathrm{pl} : \mathbb{R}_+ \to \mathbb{R}_+$ the principal branch of the inverse mapping of $x \to xe^x$.

Theorem 3. *There exists* $r_{\rm eff} > 0$, $c_{\rm eff} > 0$ *and* $C_{\rm eff} > 0$ *such that if* $0 < r < r_{\rm eff}$ *and* $\mathrm{pl}(r^{-1})^2 \geq d_{\rm eff}(\zeta) := \mathrm{dist}\,(\zeta, \mathrm{spect}\, H_{\rm eff}) \geq c_{\rm eff}\, r\, \mathrm{pl}(r^{-1})$ *then* $\zeta \in \rho(H)$ *and*

$$\|(H - \zeta)^{-1} - (H_{\rm eff} - \zeta)^{-1} \Pi_{\rm eff}\| \leq C_{\rm eff} \frac{r\, \mathrm{pl}(r^{-1})^2}{d_{\rm eff}(\zeta)^2}.$$

3. Conclusion

We have proposed a perturbative method which is able to give the leading behaviour as r tends to zero of all negative eigenvalues of H as well as of its corresponding eigenvectors. For the ground state the delta model H_δ is sufficient. For the excited states it is necessary to use the Coulomb model and to determine the behaviour of its negative eigenvalues. It would be rather easy to compute the next terms in these asymptotics as long as the influence of the higher transverse modes does not manifest itself.

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