

Rydberg Excitons Journal Club Talk

November 7, 2016

1 Hydrogen scaling laws and basic equations

1.1 Two particle bound state

1.1.1 Hamiltonian

$H = \frac{p^2}{2\mu} + \frac{e^2}{\epsilon r} + \frac{P^2}{2\mu}$ where $\mu = \frac{m_1 m_2}{m_1 + m_2}$, where p is relative momentum and P^2 is the total momentum

1.1.2 Rydberg series

$E_n \approx -\frac{1}{2} m_e c^2 \alpha^2 \frac{\mu_r}{\epsilon_r^2} \frac{1}{n^2}$, defining $\mu_r = \frac{\mu}{m_e} = \frac{m_n}{m_n + m_e}$ as the relative effective mass.

In this equation, $\frac{1}{2} m_e c^2 \alpha^2 = 13.6$ eV and $\frac{\mu_r}{\epsilon_r^2} \approx 1$ for Hydrogen in free space. Positronium results in $\mu_r \sim \frac{1}{2}$, so the energy scale is reduced to 6.8 eV.

1.1.3 Wave-functions

$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$, where $a_0 = \frac{\hbar}{m_e c \alpha} \frac{\epsilon_r}{\mu_r}$

Here, $\frac{\hbar}{m_e c \alpha} \approx 0.53A$, which is the case for $\frac{\epsilon_r}{\mu_r} = 1$, i.e. Hydrogen in free space. Positronium again has $\mu_r \sim \frac{1}{2}$, so the Bohr radius increases to about 1 Å. Crucially, the wave-function for positronium is electron-positron symmetric. The only difference is an anti-correlation such that if you measure the electron and find it at (r, θ, ϕ) then the positron should be at $(r, -\theta, -\phi)$.

$$\psi_{200} \sim \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\psi_{210} \sim z e^{-r/2a_0}$$

$$\psi_{21\pm 1} \sim \rho e^{\pm i\phi} e^{-r/2a_0}$$

1.1.4 Other typical n-scalings

$$\Delta E \sim n^{-3}$$

$$\langle r \rangle = a_0^* n^2, \langle \sigma \rangle \sim n^4, \langle V \rangle \sim n^6$$

$$\text{Dipole moment } \langle n d | e r | n f \rangle \sim n^2$$

$$\text{Polarizability } \alpha \sim n^7$$

$$\text{Radiative lifetime } n^3$$

1.2 Rydberg atom

1.2.1 Definition

For an atom with $Z > 1$, a neutral state in which the highest energy electron has an energy much higher than the ground state, while still unionized. The key feature is that the energy series for such large principle quantum numbers n , the energy spectrum reduces back to the old Rydberg formula with small corrections called quantum defects, which cause the series to be proportional to $\frac{1}{(n-\delta)^2}$, where δ is the defect term, which is usually less than 1. It is related to the polarizability of the core (an attractive $\frac{1}{r^4}$ term) as well as the deviation from a r^{-1} potential at small r , causing more tightly bound states for small angular momenta.

1.2.2 Typical characteristics / Why interesting

The main characteristics of a Rydberg atom are those of an atom with large principle quantum number n

- Large average orbital radius, as much as a micron for $n \sim 200$
- Small energy splittings between neighboring states. $\sim meV$ for typical Rydberg atoms
 - Long relaxation times due to unlikeliness of radiative relaxation***
 - Otherwise “small” perterubations can be very large in this case (see next full bullet)
- Sensitive to environment
 - Highly polarizable
 - * Easily ionizable by external electric fields
 - * Can study both diabatic and adiabatic behavior of energy levels w/ $\vec{E}(t)$
 - * Interacts with other atoms in interesting ways
 - Magnetic fields have a strong effect on the orbit – geometric cross section can encompass many flux quanta.
- Quantum information – long relaxation times, etc

1.2.3 Oscillator strength

Strength of the dipole coupling to light. Determined by integral of the absorption/emission peak.

1.2.4 Quantum Defect

Correction to the Rydberg series, the δ term in $\frac{1}{(n+\delta)^2}$. δ is usually negative, and is largest in magnitude for states with small l . Usually negligible for f orbitals and higher.

For atoms, this comes from the polarizability of the valence electron cloud around the nucleus as well as penetration of the wave-function to the core, resulting in stronger binding energies s and p states. I couldn't find any papers for this on positronium, but presumably it does exist due to the fact that the wave-function of the positron can be warped then a defect term exists.

For excitons, there also exist defect terms, but they are of different origin than for atoms. In low-dimensional systems (such as nanotubes and TMDs) the anti-screening effect results in a positive defect-like effect.

2 Excitons in General

2.1 Effective Mass Approximation – single particle

Write down Bloch and Wannier equations:

$$|b_k(r)\rangle = \frac{1}{\sqrt{N}} \sum_k e^{ikR} |w(r - R_j)\rangle \quad (1)$$

$$|w(r - R_j)\rangle = \frac{1}{\sqrt{N}} \sum_r e^{-ikR} |b_k(r)\rangle \quad (2)$$

Then write down your hamiltonian, with Bloch eigenstates:

$$[H_0 + H_1(r)] \Psi = E\Psi \quad (3)$$

and expand the eigenfunction

$$\Psi(r) = \sum_j F(R_j) |w(r - R_j)\rangle \quad (4)$$

and left-multiply a wannier function at j' :

$$\sum_j \langle w(r - R_{j'}) | H_0 F(R_j) | w(r - R_j) \rangle + \sum_j \langle w(r - R_{j'}) | H_1 F(R_j) | w(r - R_j) \rangle = \xi \sum_j \langle w(r - R_{j'}) | F(R_j) | w(r - R_j) \rangle \quad (5)$$

but since $F(R_j)$ only depends on an index, then we can pull it out :

$$\sum_j \langle w(r - R_{j'}) | H_0 | w(r - R_j) \rangle F(R_j) + \sum_j \langle w(r - R_{j'}) | H_1 | w(r - R_j) \rangle F(R_j) = \xi \sum_j \langle w(r - R_{j'}) | w(r - R_j) \rangle F(R_j) \quad (6)$$

$$\sum_j \langle w(r - R_{j'}) | H_0 | w(r - R_j) \rangle F(R_j) + \sum_j \langle w(r - R_{j'}) | H_1 | w(r - R_j) \rangle F(R_j) = \xi \cdot F(R_{j'}) \quad (7)$$

$$\sum_j H_0^{jj'} F(R_j) + \sum_j H_1^{jj'} F(R_j) = \xi \cdot F(R_{j'}) \quad (8)$$

Now if we assume that the perturbing potential $H_1(r)$ varies slowly in space, then we can assume that the perturbing term in eqn 8 only works for $j = j'$ and we take $H_1(r)$ to get

$$\sum_j \langle w(r - R_{j'}) | H_1(r) | w(r - R_j) \rangle \approx H_1(R_{j'}) \quad (9)$$

$$\sum_j H_0^{jj'} F(R_j) + H_1(R_{j'}) \cdot F(R_{j'}) = \xi \cdot F(R_{j'}) \quad (10)$$

We can see that the final thing we want is for

$$\sum_j \langle w(r - R_{j'}) | H_0 | w(r - R_j) \rangle F(R_j) = E(k) F(R_{j'}) \quad (11)$$

so choose $r = r - R_{j'}$:

$$\sum_j \langle w(r) | H_0 | w(r - (R_j - R_{j'})) \rangle F(R_j) = E(k) F(R_{j'}) \quad (12)$$

$$\sum_j h_0(R_j - R_{j'}) \cdot F(R_j) = E(k) F(R_{j'}) \quad (13)$$

$$\sum_j h_0(R_j) \cdot F(R_j - R_{j'}) = E(k) F(R_{j'}) \quad (14)$$

And we note that:

$$F(R_j - R_{j'}) \approx e^{-R_j \vec{\nabla}_{R_{j'}}} F(R_{j'}) \quad (15)$$

to get

$$\sum_j h_0(R_j) \cdot e^{-R_j \vec{\nabla}_{R_{j'}}} F(R_{j'}) = E(k) F(R_{j'}) \quad (16)$$

$$\left[\sum_j h_0(R_j) \cdot e^{-R_j \vec{\nabla}_{R_{j'}}} \right] F(R_{j'}) = E(k) F(R_{j'}) \quad (17)$$

where the second line emphasizes that the envelope function has been taken out of the summation. The final thing to note is that the bracketed term has a very useful reduction

$$\sum_j h_0(R_j) \cdot e^{-R_j \vec{\nabla}_{R_{j'}}} = \frac{\hbar^2}{2m_{eff}} \nabla_{R_j}^2 \quad (18)$$

which comes from the following deductions:

$$E(k) = \langle b_k | H_0 | b_k \rangle \quad (19)$$

$$= \frac{1}{N} \sum_{j,j'} e^{-ik(R_j - R_{j'})} h_0(R_j - R_{j'}) \quad (20)$$

$$= \sum_j h_0(R_j) e^{-iR_j k} \quad (21)$$

where the last step comes from recognizing that a sum over all j' is the same for any j , so a factor of N goes out front and cancels. An equivalent statement is that $R_j - R_{j'} \rightarrow R_{j''}$ and we counted each term N times.

So ultimately we see the correspondence where $k \leftrightarrow i\vec{\nabla}_{R_j}$, and get:

$$E(i\vec{\nabla}_{R_{j'}})F(R_{j'}) + H_1(R_{j'}) \cdot F(R_{j'}) = \xi \cdot F(R_{j'}) \quad (22)$$

$$E(i\vec{\nabla})F(r) + H_1(r) \cdot F(r) = \xi \cdot F(r) \quad (23)$$

$$\left[-\frac{\hbar^2}{2m_{eff}} \nabla^2 + qV(r) \right] F(r) = \xi \cdot F(r) \quad (24)$$

And this is how we get a hydrogen-like Hamiltonian for a smoothly varying perturbative potential in a semiconductor in what we call the effective mass approximation.

2.2 Two particles

Plots from Yu and Cardona on page 268 and 271.

Solve with Wannier functions again, but now with two states (electron and hole)

$$\psi(r_e, r_h) = N^{-1} \sum_{R_e R_h} \Phi(R_e, R_h) w_e(r_e - R_e) w_h(r_h - R_h). \quad (25)$$

The envelope function Φ , again via the effective mass approximation ends up with the same form as positronium/Hydrogen

$$H = -\frac{\hbar^2}{2m_e} \nabla_{R_e}^2 - \frac{\hbar^2}{2m_h} \nabla_{R_h}^2 - \frac{e^2}{\epsilon_0 |R_e - R_h|} \quad (26)$$

$$H\Phi = E\Phi \quad (27)$$

By using the same tricks as for the Hydrogen atom (CoM reference frame, separation of variables), we can solve this to get the same functional form for energy eigenvalues and

$$E_n \approx -\frac{1}{2} m_e c^2 \alpha^2 \frac{\mu_r}{\epsilon_r^2} \frac{1}{n^2} \quad (28)$$

where $\mu_r = \frac{\mu}{m_e} = \frac{1}{m_e} \frac{m_{cb} m_{vb}}{m_{cb} + m_{vb}}$ is the ‘‘relative effective mass’’ and $\frac{1}{2} m_e c^2 \alpha^2 = 13.6$ eV.

2.3 When does it follow the Rydberg series?

For large n values, it follows the Rydberg series with a defect correction. For small n values, the Wannier solution may not apply if the Bohr radius is small compared to the gradient of the perturbing potential. Errors are larger for more ionic materials (larger band-gaps, more localized excitons).

2.4 Selection rules (Bloch states and s- vs p-excitons)

Laporte Rule determines whether an electric-dipole transition is allowed. The primary need is for a change in parity between the initial and final state of the transition. In atoms, this prevents $s - s$ orbital transitions

and $p - p$ orbital transitions, but allows $s - p$ and $p - s$ transitions. For a single-photon transition, the angular quantum number must change by magnitude of 1.

The situation in a semiconductor is different. Bands in general have the character of a particular atomic orbital's parity. The presence of a basis may further change that for a given band (e.g. molecular orbitals can go from negative to positive parity). Moreover, this only truly applies at zero momentum – at finite momentum, the envelope wave-function (the wave-like part) mixes things. This is because the Bloch wavefunction looks something like

$$\psi_{kn}(r) = e^{ik \cdot r} u_{0n}(r) \quad (29)$$

so at $k = 0$ then

$$\psi_{0n}(r) = u_{0n}(r) \quad (30)$$

which has a well-defined parity.

image of bands with orbital label

GaAs

Conduction band is s -like and the valence bands are p -type. This means direct excitation across the single-particle gap is allowed, and s -type excitons are the most easily seen.

Cu2O

The copper d -orbitals are the dominant contributor to the exciton series in question, and the bottom CB and top VB are both of positive symmetry. This means the exciton to be measured must have negative symmetry, so the p -states are the only ones observed via electric dipole transitions. The $1S$ state is also observed, which is excited via electric quadrupole or magnetic dipole transition; as such, it has a very narrow linewidth.

1H-MoS2

The VB and CB have a mixture of d - and p -orbital character (but mostly d -), and due to the strong breaking of inversion symmetry, parity is a particularly bad quantum number here. It turns out that the s -type excitons are still most strongly observed since the dipole-allowed transitions dominate the absorption spectrum.

Graphene

The VB and CB are related to chemistry as the bonding and anti-bonding molecular orbitals. These have positive and negative parity, respectively. As a result, transitions between the bands in graphene are electric-dipole allowed. (Strictly speaking this would only apply right at the K-points, but the idea is there).

2.5 Dipole blockade

E-field from a dipole = $\vec{E} = \frac{1}{4\pi\epsilon} \frac{3(\vec{p} \cdot \hat{r})\hat{r} - \vec{p}}{r^3} - \frac{1}{3\epsilon} \vec{p} \delta^3(r)$ which is linear to dipole moment and proportional to r^{-3}

Potential energy between two dipoles is $V = -\vec{p} \cdot \vec{E} = \frac{1}{2\pi\epsilon} \frac{(\vec{p}_1 \cdot \vec{r})(\vec{p}_2 \cdot \vec{r})}{r^3} \propto \frac{p_1 p_2}{r^3}$

2.5.1 Dipolar Interaction

Interaction between induced dipole moments will go something like the dipole-dipole interaction:

$$V_{dd} \sim p_1 p_2 \cdot R^{-3} \sim n^4 \cdot R^{-3} \quad (31)$$

The interaction energy between two induced dipoles is second order when in the non-degenerate limit and so

$$\Delta E_{vdW} \propto \frac{|V_{dd}|^2}{\Delta} \propto \frac{(n^4/R^3)^2}{n^{-3}} \propto \frac{n^{11}}{R^6} \quad (32)$$

For the case that V_{dd} is very large, then the energy separation between the Rydberg states can be considered to be degenerate and then

$$\Delta E_F \propto V_{dd} \propto \frac{n^4}{R^3} \quad (33)$$

2.5.2 Dipole Blockade Radius / Volume

We choose that the blockade volume occurs when the change in energy is roughly the same as the linewidth of a given state. Remembering that $\Gamma_n \sim n^{-3}$ we find that

$$V_{blockade} = \frac{4}{3}\pi R^3 \quad (34)$$

$$= \frac{4}{3}\pi C \frac{n^4}{\Delta E_F} \quad (35)$$

$$= \frac{4}{3}\pi C \frac{n^4}{\hbar\Gamma_n/2} \quad (36)$$

$$\propto n^7 \quad (37)$$

which has the same scaling as the polarizability, as we might expect.

They did some detailed calculations to estimate the coefficient and found $C = 6 \times 10^{-4} \mu eV \cdot \mu m^3$, resulting in

$$V_{blockade} \approx n^7 \cdot 3 \times 10^{-7} \mu m^3. \quad (38)$$

Transforming this to a blockade radius:

$$R_{blockade} = \sqrt{\frac{3}{4\pi} V_{blockade}} \quad (39)$$

$$= 7nm \cdot n^{7/3} \quad (40)$$

noting that this increases slightly more quickly than the actual radius.

As a ratio to the actual exciton radius:

$$\frac{R_{blockade}}{\langle r \rangle} = \frac{7nm \cdot n^{7/3}}{7.5nm \cdot n^2} \approx 1 \cdot n^{1/3} \quad (41)$$

NOTE: using the vdW instead of the Forster interaction gives the same scaling, albeit with perhaps a different coefficient:

$$\Delta E_{vdW} \sim \frac{n^{11}}{R^6} \sim \hbar\Gamma_n \sim n^{-3} \quad (42)$$

$$R^6 \sim n^{14} \quad (43)$$

$$V \sim R^3 \sim n^7 \quad (44)$$

3 This paper

3.1 Overview of Cu2O

Picture of crystal structure and band structure, including symmetries and all the exciton series. We focus here on the yellow series, which is the lowest energy series. As noted, only p-excitons are easily observed, since they are dipole allowed.

$$\varepsilon_r = 7.5$$

3.2 Lineshapes:

3.2.1 Lorentzian, symmetric (homogenous)

This is the usual form for a naturally broadened spectral line.

$$\alpha_n(E) = C_n \frac{\frac{\Gamma_n}{2}}{\left(\frac{\Gamma_n}{2}\right)^2 + (E - E_n)^2} \quad (45)$$

3.2.2 Lorentzian, asymmetric (homogenous)

The absorption line in this system is asymmetric as per the following formula.

$$\alpha_n(E) = C_n \frac{\frac{\Gamma_n}{2} + 2q_n(E - E_n)}{\left(\frac{\Gamma_n}{2}\right)^2 + (E - E_n)^2} \quad (46)$$

where q_n is the asymmetry parameter.

3.2.3 Gaussian (inhomogenous)

Random distribution of energies according to some paramter (e.g. disorder potential) leads to a Gaussian smearing.

3.3 n-scaling

$E_n \sim n^{-2}$ as expected, including a defect of $\delta = -0.23$

FWHM $\sim n^{-3}$, so lifetime goes as n^3

Oscillator strength $\sim n^{-3}$

3.4 Blockade effects, $n = 24$

Reduction of absorption at $100 \mu W$ of absorbed laser power, which for $1 ns$ lifetimes means about $100 fJ$ energy in that time. For an exciton energy of $2 eV$ this means $300,000$ excitons in a volume of $300 \mu m^3$, from which you get a blockade radius of $5 \mu m$.

The absorption changes due to blockade will be reduced by a factor $1 - \rho_{ex} V_{blockade}$, where ρ_{ex} is the number density of the excitons and V_{block} was derived earlier:

$$\alpha = \alpha_0 (1 - \rho_{ex} V_{block}) \quad (47)$$

and the exciton density is determined by the absorption itself with the laser power and exciton lifetime:

$$\rho_{ex} = \frac{P_L \alpha T_1}{\hbar \omega A_{spot}} \quad (48)$$

$$\alpha = \alpha_0 \left(1 - \frac{P_L \alpha T_1}{\hbar \omega A_{spot}} V_{block} \right) \quad (49)$$

which we can solve:

$$1 = \frac{\alpha_0}{\alpha} - \frac{P_L \alpha_0 T_1 V_{block}}{\hbar \omega A_{spot}} \quad (50)$$

$$\frac{\alpha}{\alpha_0} = \frac{1}{1 + \frac{T_1 \alpha_0 V_{block}}{\hbar \omega A_{spot}} P_L} \quad (51)$$

$$\frac{\alpha}{\alpha_0} = \frac{1}{1 + S_n P_L} \quad (52)$$

where

$$S_n = \frac{T_1 \alpha_0 V_{block}}{\hbar \omega A_{spot}} \quad (53)$$

3.5 Magnetic field effect on positronium [incomplete]

Introducing a strong magnetic field can decrease the overall size of the Rydberg atom. The magnetic length

$$l_B = \sqrt{\frac{\hbar}{eB}} = \frac{25nm}{\sqrt{B/1T}} \quad (54)$$

so for $B = 0.8T$ the length is about 29 nm.

4 Appendices

4.1 General optical stuff:

$$R = \left| \frac{n-1}{n+1} \right|^2$$

4.2 Gapped Graphene

Dispersion: $E = \pm (\delta^2 + \hbar^2 v^2 k^2)^{\frac{1}{2}}$, so the gap at $k = 0$ is $E_g = 2\delta$. Here, $v \approx \frac{c}{300}$.

The Fermi velocity is $v_F = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \frac{\hbar v^2 k}{(\delta^2 + \hbar^2 v^2 k^2)^{\frac{1}{2}}}$.

The effective mass is $\frac{1}{m_{eff}} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} = \frac{v^2}{(\delta^2 + \hbar^2 v^2 k^2)^{\frac{1}{2}}} - \frac{\hbar^2 v^4 k^2}{(\delta^2 + \hbar^2 v^2 k^2)^{\frac{3}{2}}}$.

The effective mass at $k = 0$ is $m_{eff}(0) = \frac{\Delta}{v^2}$.

The energy series for 2D positronium is $E_{ex} = -13.6 \cdot \frac{\mu_r}{\varepsilon_r^2} \frac{1}{(n - \frac{1}{2})^2}$. Here, we choose $\mu_r = \frac{1}{2} m_{eff}(0) / m_e$ since gapped graphene should be particle-hole symmetric. This gives an exciton binding energy

$$E_{ex} = -6.8 \frac{\delta}{v^2 m_e \varepsilon_r^2} \frac{1}{(n - \frac{1}{2})^2} \quad (55)$$

It turns out that $\frac{6.8eV}{(\frac{c}{300})^2 m_e} \approx 1.2$. So $E_{ex} \approx -1.2 \cdot \delta \frac{1}{\varepsilon_r^2 (n - \frac{1}{2})^2}$. The energy difference between the single particle energy gap and the exciton energy series is

$$\Delta E_n = E_g - |E_{ex}| = 2\delta \cdot \left(1 - \frac{0.6}{\varepsilon_r^2 (n - \frac{1}{2})^2} \right) \quad (56)$$

If this number is negative, then there exists an instability. For $n = 1$ and 2 the factor $(n - \frac{1}{2})^{-2} = 4$ and $\frac{4}{9}$, respectively.

$$\Delta E_1 = 2\delta \left(1 - \frac{2.4}{\varepsilon_r^2} \right) \quad (57)$$

$$\Delta E_2 = 2\delta \left(1 - \frac{4}{15\varepsilon_r^2} \right) \quad (58)$$

Restricting $\varepsilon_r \geq 1$, it is clear that for any $n \geq 2$ that the single particle gap is always larger. For $n = 1$, negative values appear possible. We can find the zero-energy point at $\Delta E_1 = 0$, which occurs at

$$\varepsilon_r = \sqrt{2.4} \approx 1.55 \quad (59)$$

This would explain why for most moire-gapped graphene systems that the excitonic instability is probably not important. In these systems there are two components that increase ε_r . First is the h-BN substrate that exists beneath the graphene. This usually results in the relative permittivity relevant to the 2D electrons to be the mean of that above and below. The relative permittivity of h-BN is estimated to be in the range $\varepsilon_{hBN} \sim 3 - 4$, so that puts $\varepsilon_r \sim 1.5 - 2$, which is just on the upper limit necessary for the instability to be relevant. The second feature of the devices is that a gate electrode typically exists nearby to the graphene,

usually within 5-25 nm, which will further increasing the screening. So for moire-gapped graphene, the instability is unlikely to be relevant.

However, we can obtain $\epsilon_r \approx 1$ for suspended graphene. Perhaps placing graphene on just a few (between 1 and 3) layers of h-BN with a small twist angle (to generate the moire gap) and suspending the entire structure would be sufficient to obtain this.

The principle limitation of the above back-of-the-envelope calculations is that the low- n excitons are generally do NOT follow the Rydberg series due to the breakdown of the ability to use Wannier functions in the analysis (i.e. the above formulation works best for high- n energy levels / extended states).