Summary of our Numeric Solution to the Schrödinger Equation for Holes of Bound Excitons in ZnO

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(Dated: June 18, 2020)

Abstract

We developed a Python 3 program that solves the Schrödinger equation for holes of bound excitons in ZnO. To do so, we implemented the shooting and bisection method, and used the Verlet algorithm to give the wavefunction for each guess of the energy. In this report we describe these methods in detail and present some key results. The application of these methods was first developed and verified using the hydrogen potential, before implementing both the Puls and Kratzer potential for the ZnO exciton calculations. For the hydrogen potential, we have shown high accuracy in the eigenenergies, with an error of less than 0.2%. For the Puls and Kratzer potential, we varied the effective mass through the parameter 'K' and obtained energy levels which vaguely correspond to experimental data for the Ga impurity. Interpretation of these results will likely be discussed in a later summary this summer. Much of the ground work was completed by Matthew Frick, who wrote the first version of this code in Julia.

I. WHERE TO ACCESS THE SOURCE CODE

The programs were coded in jupyter notebook (https://sfu.syzygy.ca) Python 3 files. Copies of these files can be found in the remote Github repository: https://github.com/simwat/symphony. The folder 'Bound_Excitons_Energy' contains the latest code named: June3_PulsPotential_K_parameter_Ga_n=4_Documentation.ipynb. Here we will mostly go through the first section.

Instructions to the push and pull files between the repository and jupyter notebooks are documented in the .txt file Syzygy_To_Github_Instructions, also found in the repository.

II. PULS POTENTIAL UNIT CONVERSION

We first state the radial component of the Schrödinger equation,

$$\frac{1}{r}\frac{d^2}{dr^2}(r\psi) = \frac{2m}{\hbar^2}\left(-E + V(r)\right)\psi \quad . \tag{1}$$

Following a derivation preceding Eq. 19.46 in the online Feynman lecture [1], the orbital angular momentum is added to the equation as such,

$$\frac{1}{r}\frac{d^2}{dr^2}(r\psi) = \frac{2m}{\hbar^2}\left(-E + V(r) + \frac{l(l+1)\hbar^2)}{2mr^2}\right)\psi \quad . \tag{2}$$

For the bound exciton, the Puls potential is written as

$$V(r) = \frac{-e^2}{\epsilon_0 r_h}[1 - 2e^{\frac{-2r_h}{a_e}}(1 + \frac{r_h}{a_e})] \quad . \tag{3}$$

Here, r_h is the position of the hole, and a_e is effective Bohr radius subject to the donor atom and its number of electrons. There are now a few relations needed to eliminate constants and to recast certain variables. First, the acceptor and donor Bohr radii are respectively defined as,

$$a_A = \frac{\hbar^2}{m_h e^2} \quad , \tag{4a}$$

$$a_D = \frac{\hbar^2}{m_e e^2} \quad , \tag{4b}$$

where m_h and m_e are the effective hole and electron masses. In atomic units, $m_h = 0.59$ and $m_e = 0.28$ in ZnO [2]. Similarly, the acceptor and donor Rydbergs are define as,

$$Ry_h = \frac{m_h e^4}{2\hbar^2} \quad , \tag{5a}$$

$$Ry_e = \frac{m_e e^4}{2\hbar^2} \quad . \tag{5b}$$

Since the effective Bohr radius must be a variable parameter, it can be written as,

$$a_e = K a_D \quad . \tag{6}$$

Here, K is an adjustable parameter. To simplify the unit of position to that of hole Bohr radius, we scale r_h with,

$$\rho_h = \frac{r_h}{a_A} \quad . \tag{7}$$

Similarly, we scale the energy to be in units of acceptor Rydbergs with,

$$\epsilon = \frac{E}{Ry_h} \quad . \tag{8}$$

With substitutions from the above relations, the Puls potential becomes,

$$V(\rho_h) = \frac{-2}{\rho_h}[1 - 2e^{-2\rho_h a_A/a_e}(1 + \rho_h a_A/a_e)] \quad . \tag{9}$$

Further simplifications lead to,

$$V(\rho_h) = \frac{-2}{\rho_h}[1 - 2e^{-2\rho_h m_e/(K m_h)}(1 + \rho_h m_e/(K m_h))] \quad , \tag{10}$$

where the potential is in acceptor Rydbergs units, with all known variables.

Using the same substitutions on Eq. 2, considering $r = r_h$ and converting to units of hole Bohr radii and acceptor Rydbergs, the radial Schrödinger equation for the hole becomes,

$$\frac{d^2(\rho_h \psi)}{d\rho^2} = \left(-\epsilon + V(\rho_h) + \frac{l(l+1)}{\rho_h^2}\right)\rho_h \psi \quad . \tag{11}$$

Notice that this is a second order ODE of the product $\rho_h \psi$. Casting this product as a new variable f, we obtain,

$$\frac{d^2(f)}{d\rho^2} = \left(-\epsilon + V(\rho_h) + \frac{l(l+1)}{\rho_h^2}\right) f \quad . \tag{12}$$

This is the form of the equation used to solve for the wavefunctions. The associated eigenenergies can be converted to eV units from acceptor Rydbergs by,

$$Ry_h = \frac{m_h}{m_e} \frac{m_e}{\epsilon^2} Ry = \frac{0.59}{8.5^2}(13.6 \ eV) = 0.111 \ eV \quad . \tag{13}$$

Here,

$$\frac{m_h}{m_e} \quad , \tag{14}$$

is the conversion factor between Ry_e and Ry_h. Similarly the factor

$$\frac{m_e}{\epsilon^2} \quad , \tag{15}$$

is the conversion factor from Ry_e to effective Rydbergs.

III.   VERLET FUNCTION

The Verlet algorithm was chosen as the wavefunction generator for this problem because it does not require the initial values of a trajectory to calculate the rest of it. If the initial values were known, it would be simpler to use a built-in ivp solver. Instead, the Verlet algorithm only relies on the knowing values of any two points to generate the full trajectory. As quick derivation of the Verlet algorithm follows.

We take the system of taylor expansions:

$$f(\rho + d\rho) = f(\rho) + dx f'(\rho) + \frac{dx^2 f''(\rho)}{2!} + \frac{dx^3 f'''(\rho)}{3!} + ... \quad , \tag{16a}$$

$$f(\rho - d\rho) = f(\rho) - dx f'(\rho) + \frac{dx^2 f''(\rho)}{2!} - \frac{dx^3 f'''(\rho)}{3!} + \quad . \tag{16b}$$

Adding $f(\rho + d\rho)$ and $f(\rho - d\rho)$ together gives,

$$f(\rho + d\rho) + f(\rho - d\rho) = 2f(\rho) + 2\frac{dx^2 f''(\rho)}{2!} \quad . \tag{17}$$

After rearranging, the equation becomes,

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$$f(\rho - d\rho) = 2f(\rho) - f(\rho + d\rho) + 2\frac{dx^2 f''(\rho)}{2!} \quad . \tag{18}$$

Notice that our Schrödinger equation is a second order ODE given by,

$$f''(\rho) = \left(-\epsilon + V(\rho_h) + \frac{l(l+1)}{\rho_h^2}\right) f \quad . \tag{19}$$

And so replacing the $f''(\rho)$ in the integration equation gives,

$$f(\rho - d\rho) = 2f(\rho) - f(\rho + d\rho) + dx^2 \left(-\epsilon + V(\rho_h) + \frac{l(l+1)}{\rho_h^2}\right) f \quad . \tag{20}$$

Thus, if we know a value $f(\rho + d\rho)$ and the value before that, $f(\rho)$, we will know the value at an even earlier point, $f(\rho - d\rho)$.

This allows us to integrate the wavefunction backwards since we know the end values (zero and close to zero) for spherically symmetric potentials.

IV.   SHOOTING AND BISECTION

The main body of our eigenvalue solver employs the shooting and bisection method. At the core, this code checks the guess solutions generated by the Verlet function and modifies the guess. It does this iteratively until the boundary condition (f(0) = 0) is satisfied to specified tolerance level.

A.   Below are some of the variables explained:

- K is a parameter that varies the effective mass of the electron and consequently the potential. For each value of K specified, a complete set of correct eigenvalue energies and wavefunctions ($\rho\psi$) will be generated.

- En and f_nl are the list variables that hold the solutions of each orbital, for a given K. They have the same length as the number of orbitals specified. f_nl is two dimensional, where its x length is that defined for ρ.

- Etot is the nested list that will holds En for all given K. It is the analogue of a cell in MATLAB. The nested loop appends K-1 more zeros to each initial element of zero. Each element is then converted to the type float.

- delta holds the numeric difference between the guess solution's boundary value and the required boundary condition. It has a length of two so as to compare two consecutive guess solutions.

- E1 and E2 hold the eigenvalue guesses each time the Verlet function generates a guess solution for a particular orbital. E1 is set initially as the lower bound of all the energies in acceptor Rydbergs. The value of -1.1 was set because of the previous computation of the hydrogen energy values. Through an increment of dE = 0.001 from E1, E2 holds an eigenvalue guess that has stepped towards the correct eigenvalue.

- E is a third eigenvalue variable that is mainly needed to hold the succeeding guess determined from the bisection method. It also holds the latest eigenvalue that should will be tested by the Verlet function, even before bisection starts.

- BC_0 is a constant representing the boundary condition of zero at $\rho = 0$. This must be true for a physical wavefunction $\rho\psi$.

- tolerance_min is a constant that determines how close the boundary value must be to the required boundary condition in order for the solution to be accepted as correct.

- Bisecting is a boolean that indicates if the eigenvalue guess is to be stepped forward by bisection or just by increment. Bisecting is set to false initially because the initial guess is far from the solution.

- n is the principal quantum number and is manifested here as an index.

- f holds one wavefunction guess generated by the Verlet function for a particular K, orbital angular momentum l, and eigenvalue guess. n is not explicitly a Verlet function parameters because it is already assigned to an eigenvalue solution by virtue of being the index.

- count is the index that indicates the position in the lists of En and f_nl in which the eigenvalue energy solutions for each orbital will be saved. count is set back to zero for the start of each iteration of K.

- E2_moved is a boolean that indicated whether E2 or E1 has been assigned the latest eigenvalue guess in the bisection routine. This information determines the next assignments to step closer to the correct solution. More about the bisection routine to come.

B. The chronological process of the code is as follows:

1. The Verlet function is called and generates a wavefunction with the initial guess E1. f holds this wavefunciton.

2. The difference between the first value the wavefunction and the boundary condition is stored in the first element of delta.

3. The possibly large number of iterations to step the eigenvalue guess forward begins:

4. Since the initial eigenvalue guess is not close to, and is much smaller than, the correct solution (by the set up of E1), Bisecting was set as false initially. Thus we step the energy by a positive increment. This is done by setting E, which will always hold the latest eigenvalue guess, to E2.

5. Verlet function is called with the latest eigenvalue guess and the wavefunction stored in f again.

6. Again, the difference between the latest wavefunction value at $\rho = 0$ and the boundary condition is calculated but stored now in the second element of delta.

7. The magnitude of this latest element of delta is then checked. At this point, it is not below the tolerance.

8. The Bisecting boolean is checked and is still set as false at this point. So the bisection code is skipped.

9. The sign of the two elements of delta are checked. At this point, they are both the same because the eigenvalue guess is not close to the correct solution.

10. What is needed is to increment the guess to a larger value. So the eigenvalue variables step forward, replacing the value of E1 with that of E2 (which is closer) and incrementing E2 itself.

11. The first element of delta steps forward to store the value of the second element of delta, leaving the latter free to store the numeric difference of the next solution generated.

12. Returning to the start of this for loop, the eigenvalue guess E is updated with the latest value of E2, and again used in the Verlet function call. The difference between the solution and requirement at the $\rho = 0$ boundary is again recorded and evaluated for convergence. As convergence is not achieved and Bisecting is False: E1, E2, and delta are again stepped forward. This step is repeated until the signs of the two delta elements are opposite.

13. At the point where the two delta elements first have opposing signs, Bisecting will be set as True for the first time (and will remain True). This means that the boundary value of the current wavefunction and of the wavefunction computed in the previous iteration are numerically straddling the required boundary condition. The energy guess will no longer need to continue to increment in the same direction and in the same amount. Instead, the bisection method is used to quickly zero-in on the boundary requirement.

14. To step up the energy variables for a successful bisection routine, E2 continues to hold the latest value of E. E2_moved is initiated as True because E2 was assigned the latest value of the eigenvalue guess, E. Regardless of the value of Bisecting, delta elements will again be stepped forward.

15. Returning to the top of the for loop, Bisecting is now True and new eigenvalue guess E will result from a bisection (midpoint) of the two previous guesses E1 and E2. This is the fastest method to zero-in on the correct solution which must be in between E1 and E2 at this point. This is in contrast to the steady increment routine where the delta elements had the same sign.

16. E from the bisection method is used to call the Verlet function, and the convergence is again evaluated. As convergence is not achieved, the bisection routine will continue as Bisecting will remain True.

17. The bisection routine mainly determines if E1 or E2 should be assigned the latest E that was tested. It assures that E1 and E2 are updated, always straddling the

correct solution and always closer to the solution than the previous iteration. The code segment starting with "if Bisecting:" is different from Matthew Frick's analogous Julia code.

18. The following explains the logic behind the "if Bisecting:" code segment:

   (a) There are three different energy guesses: E1, E2, E. The newest updated guess will always be E. The goal is to determine if E1 or E2 should have their guess value replaced by the E value. In other words, either the guess E1 or E2 will be discarded to hold the newest, updated E. This will set up E1 and E2 as successful subjects of bisection.

   (b) The elements of delta are associated with wavefunction generated by E and the immediately previous guess, either E1 or E2. The delta elements having the same sign reflects upon the latest two guesses being on the same numeric side of the correct solution.

   (c) If E2_moved is True, it means that E2 had taken the value of E last and that E2 holds the eigenvalue that corresponds to delta[0]. Then, E2 will be the immediately previous guess to E. If E2_moved is False, then E1 is the immediately previous guess to E.

   (d) The idea is to re-assign E1 and E2 as two guesses that numerically straddle the correct answer the most tightly. The newest guess is E, associated with delta[1], and the immediately previous guess is associated with delta[0]. If they are on the same numeric side as the solution, one of them should be discarded. The newest guess, E, is closer to the solution by definition of bisection, so the delta[0]-associated guess is the one discarded and re-assigned with the value of E. The third energy guess variable is guaranteed to be on the opposite side of the solution.

   (e) If the latest two guesses straddle the solution, they represent the tightest straddle. Then the third energy guess variable can be re-assigned to hold the value of E. This leave the variable E free to take on the next bisection guess.

   (f) There are four cases, described in order of the code segment:

i. Latest two guesses land on the same side of the solution and delta[0] associates with E2.

The value of E2 is replaced with E.
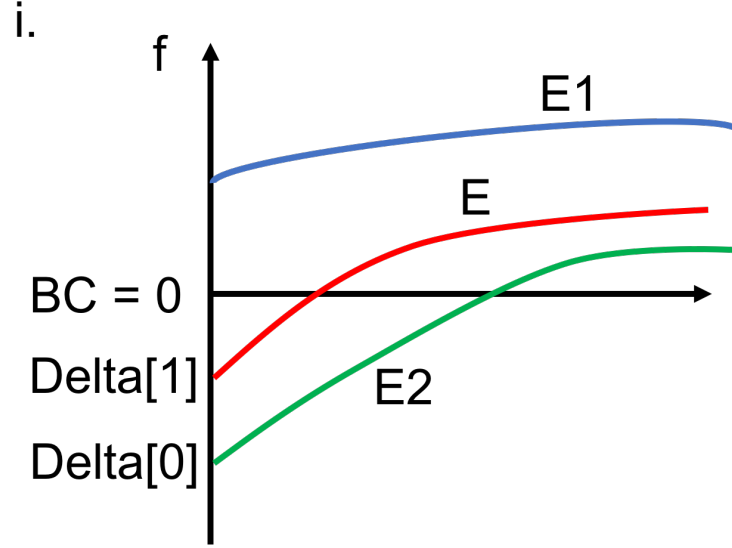
FIG. 1.   Bisection case i.

ii. Latest two guesses land on the same side of the solution and delta[0] associates with E1.

The value of E1 is replaced with E.

Assign E2_moved to False as E1 was just changed to hold E.

iii. Latest two guesses straddle the solution and delta[0] associates with E2.

The value of E1 is replaced with E.

Assign E2_moved to False as E1 was just changed to hold E.

iv. Latest two guesses straddle the solution and delta[0] associates with E1.

The value of E2 is replaced with E.

Assign E2_moved to True as E2 was just changed to hold E.

19. At this stage, E is continuously updated through bisection and used to generate new wavefunction guesses. The boundary condition convergence is evaluated each time. This to why this method is called the shooting and bisecting method: Generating wavefunctions is like shooting towards a target.

20. Once the boundary value has converged, the current eigenvalue and wavefunction are

ii.
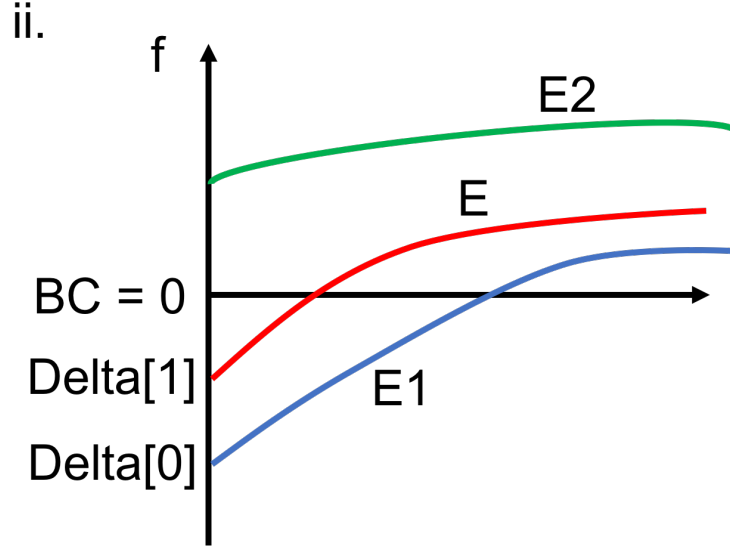
FIG. 2.   Bisection case ii.

iii.
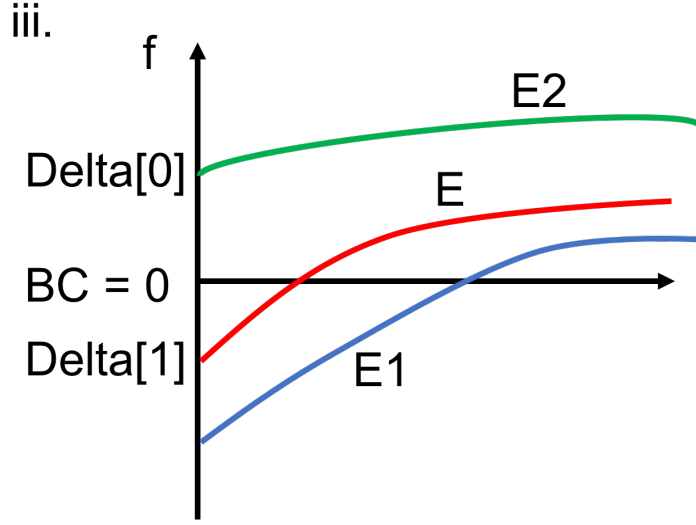
FIG. 3.   Bisection case iii.

saved in En and f_nl, for which the variable count specifies which position in the list they will be saved.

21. To prepare the energy guess variables for the next orbital, there are two options depending on the index n. If n is not at its maximum value, and the outer loop is keeping with the same value of orbital angular momentum number l, then both E1 and E2 are incremented by a small amount. In this case, the next eigenvalues are numerically larger than the current solution. However, if n is at the maximum value, this means
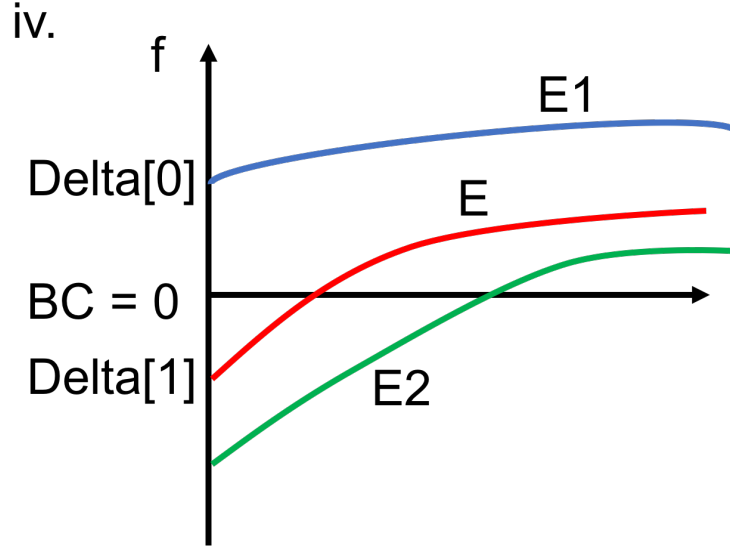
FIG. 4. Bisection case iv.

that the next eigenvalue will be smaller and thus E1 and E2 revert to the initial values of -1.1 and a small incremented amount. Lastly, the boolean Bisecting to reset to False.

22. This is repeated for each n and l, until all the specified orbitals are solved. Then the set of eigenvalues are saved in an element of Etot, specified by index associated with the current value of K.

23. Once all the values of K have a set of solved eigenvalues, then the code is complete.

24. Notes: Generally, once the code is bisecting, it will continue to bisect (Bisecting will remain True) until the wavefunction has converged. Similarly, convergence will typically not be achieved until bisection has occurred.

The rest of the code in this file is to save the Etot to an external file and to manipulate Etot into a presentable graph. This includes the conversion to meV, re-organization and extracting of relative values. A flow chart version of the shooting and bisection code is presented at the end of the report.

V.   KRATZER POTENTIAL UNIT CONVERSION

The Kratzer potential was also used the Verlet Algorithm. It is an approximation to the Puls potential and has the form of,

$$V(r_h) = -2D \left(\frac{b}{r_h} - \frac{b^2}{2r_h^2} \right) \quad , \tag{21}$$

where,

$$D = \frac{se^2}{2\epsilon_0 a_e} \quad , \tag{22}$$

and

$$b = t a_e \quad . \tag{23}$$

The parameters were set as s = 1.0136 and t = 1.337, such that the potential was best fitted to the Puls potential. Again, we seek to scale the variables to eliminate the constants. Using the same substitutions in Section II, the Kratzer potential becomes, in units of electron Rydbergs,

$$V(\rho_h) = -\frac{2s}{\rho_h} \left(t \left(\frac{m_h}{m_e} \right) - \frac{t^2 K}{2\rho_h} \left(\frac{m_h}{m_e} \right)^2 \right) \quad . \tag{24}$$

Lastly, the conversion between the electron Rydberg to effective Rydberg, then to eV, is

$$Ry_e = \frac{m_e}{\epsilon^2} Ry = \frac{0.28}{8.5^2}(13.6 \ eV) = 0.0527 \ eV \quad . \tag{25}$$

VI.   RESULTS

Tables I and II summarize the eigenvalue results from various methods at K = 1.967 and K = 1 respectively. At this time, applying the Kratzer potential to the Verlet algorithm does not yield any solutions for K = 1.9 or greater. A subset of the solutions start to be calculated for K below 1.9 and at K = 1, the full set is calculated. In Table I, the analytical Kratzer potential method uses an equation from Puls paper [3] and Eq. 28 from [2]. The computation of that equation can be found in the file named May27_KratzerPotential-DrWatkins-Convert1-AnalyticalCompare.ipynb in the Bound_Excitons_Energy folder. The analytical result is satisfactorily consistent with the computational Puls potential result.

The relative discrepancy decreases for higher orbitals.

The values are presented as relative to the ground state. The infinitely far away "orbital" had the absolute value of zero. Therefore, its relative energy is simply zero minus the (negative) ground state energy, which was also the treatment for the rest of the orbitals as well. There is a distinction between the energy of a free exciton (shown in the experimental data) and that of a hole infinitely far away from the potential.

In Table II, there is not as much consistency between the results from different methods. However, the energies seems to be in the same range and have the same behaviour. In either way, the Kratzer potential is only an approximation to the Puls potential. Some deviation is to be expected from the Puls and Kratzer computationally. There is also suspicion in the conversion method for the Kratzer potential. Interestingly, the strong consistency between the analytical and Puls computational method seen in Table I is not evident here at lower K.

1st quantum number n	2nd quantum number l	Analytic Kratzer (meV)	Puls Computational (meV)	Error b/w Puls and Analytic Kratzer (meV)	Experiment (meV)
0	0	0	0	0	0
	1	3.36388	3.94457	0.58069	6.51
	2	7.38258	8.4973	1.11472	8.83
1	0	7.78838	8.85147	1.06309	
	1	9.3544	10.64717	1.29277	10.64
	2	11.37764	12.72034	1.3427	12.3
2	0	11.59284	12.78489	1.19205	
	1	12.44501	13.68213	1.23712	
	2	13.60346	14.76534	1.16188	14.65
3	0	13.73098	14.77622	1.04524	
	1	14.245	15.28063	1.03563	
	2	14.96918	15.92377	0.95459	
free exciton	free exciton				16.04
infinity	infinity	18.89336	18.69037	-0.20299	

TABLE I. Relative eigenenergy results in meV from different methods for K = 1.967, at which point the computational results are most consistent with the experimental results for Ga. The computational Kratzer potential method did not run at this K. The energies are for the hole of a donor bound exciton in ZnO.

Figure 5 and 6 give a graphical representation of the eigenenergies with respect to K.

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1st quantum number n	2nd quantum number l	Analytic Kratzer (meV)	Krazter Computational (meV)	Puls Computational (meV)
0	0	0	0	0
	1	8.96999	6.52976	10.63977
	2	17.0786	14.39625	19.54459
1	0	15.70679	15.2839	17.60478
	1	19.21236	22.3171	24.69421
	2	22.85685	26.74139	27.07953
2	0	22.20014	22.78934	23.80654
	1	23.91756	24.45888	25.42666
	2	25.85951	26.74139	27.07953
infinity	infinity	32.1971	37.30469	31.38313

TABLE II. Relative eigenenergy results in meV from different methods at K = 1, at which point the computational results for the Kratzer potential is successfully obtained for the full set of eigenvalues. The results from the analytical method, and the computational method for both Puls and Kratzer potentials are presented.

These figures can easily show at which value of K the eigenenergies best fit with the experimental Ga impurity data, shown as solid black lines. From Fig. 5, it can be shown that the best fit is at around K = 1.96. This is the reason Table I was calculated at K = 1.967.

Figure 6 shows a larger range of K, and the energies are shown to rapidly increase a K decreases. This makes sense because a smaller K means a smaller effective Bohr radius, a_e, and a larger electron effective mass. A larger effective mass means higher energies (See equations (4) and (6)). The method of exactly fitting the computational energies with experimental ones is not concluded within this summary, however, we believe that selection rules of energies are involved. Lastly, Table III is included to show the validity of the Verlet-shooting-bisection method from calculating hydrogen energies, as the resulting energies are very close to the analytical solutions.

FIG. 5. Relative eigenenergies for 12 orbitals at distinct values of K, in the range of K = 1.90 to K = 2.00. The pink line represents a free hole, that is no longer bound. The solid black lines represent the experimental PLE energies from Ga impurities in ZnO, taken by Katrina Sterling.
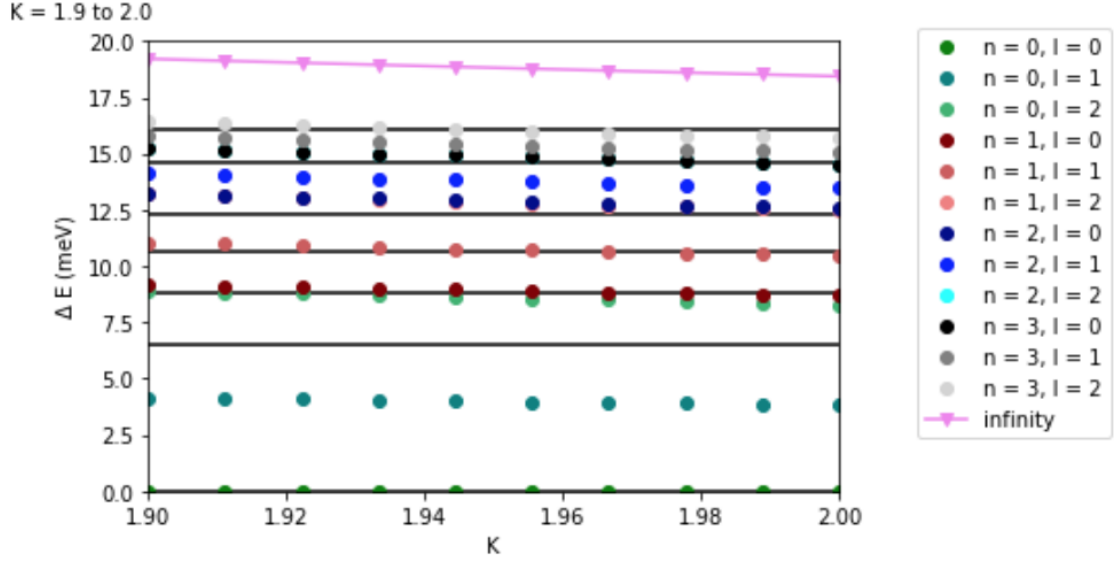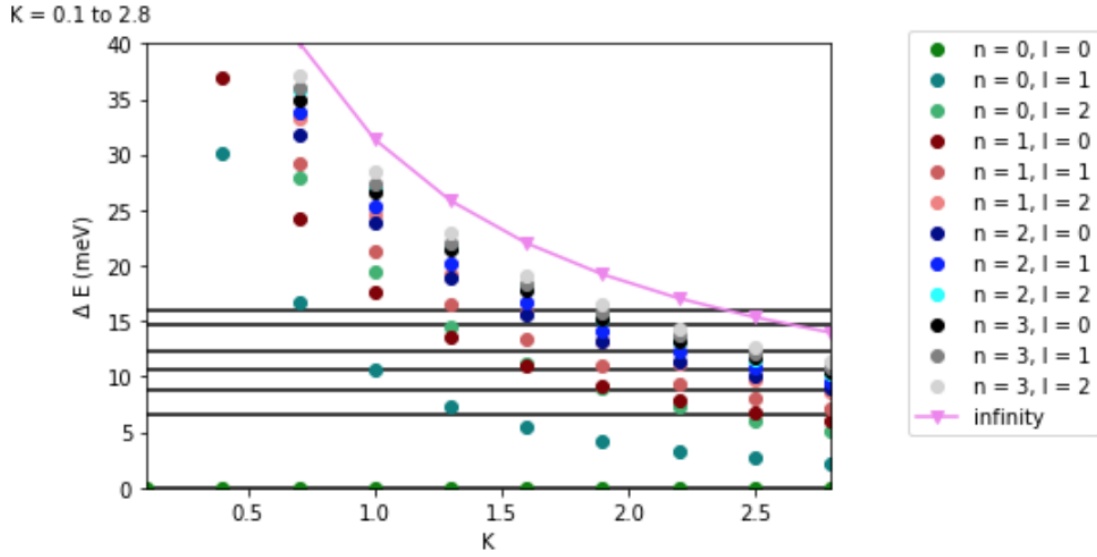

FIG. 6. Relative eigenenergies for 12 orbitals at distinct values of K, in the range of K = 0.1 to K = 2.8. The solid black lines represent the experimental PLE energies from Ga impurities in ZnO.

Physical Parameter	Numerical Value
a	0.8 nm
m	0.7 m_0

TABLE IV. The parameters given in [4] for its Eq. 2 of vibrational and rotational energy states of bound excitons. Here, m_0 is the free electron rest mass.

Orbital	Shooting Method E	Analytical E	Error E (rounded)
1s	-0.9983772766590125	-1	0.00162
2s	-0.249711090385914	-0.25	0.00029
2p	-0.24992968149504308	-0.25	0.00007
3s	-0.1109923282118761	-0.1111111111111111	0.00012
3p	-0.11105538207846964	-0.1111111111111111	0.00006
3d	-0.11108939507233535	-0.1111111111111111	0.00002

TABLE III. The eigenenergies from the shooting method as applied to the hydrogen potential, compared with the known analytical energies for hydrogen orbitals. Units in donor Rydbergs.

VII.   LITERATURE REFERENCE

The 2010 paper "Excited state properties of donor bound excitons in ZnO" by Meyer et al. [4] was examined for their theoretical model. Its Eq. 2 predicts the vibrational and rotational energies of bound excitons by analogy of molecular vibrations, and is given by,

$$E(\nu, J) = -\frac{(2ma^2/\hbar^2)D^2}{\left[(\nu + \frac{1}{2}) + \sqrt{(J + \frac{1}{2})^2 + (\frac{2ma^2}{\hbar^2})D}\right]^2} \quad . \tag{26}$$

Here, ν and J are rotational and vibrational quantum numbers respectively, D is the binding energy of the bound exciton, m is the hole band mass and a is the distance of the hole impurity. The parameter values given in the paper are summarized in Table IV.

To verify Eq. 2 with the results claimed in Meyer [4], we wrote a program in the Bound_Excitons_Energy_Folder on the Github repository, named Meyer2010_Verify_Eq2. There, the function first calculated $\frac{2ma^2}{\hbar^2}$ in inverse joules before converting to inverse meV. Then the whole expression was calculated with the five values of D given in the paper.

Tables V - IX show the replication results including the relative energies from ground state and the quoted values from the paper.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (meV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3567	-3.03175	0	0
	1	3.36574	-0.99685	2.04	2.0349
	2	3.35927	-0.46217	2.57	2.56958
1	0	3.35884	-0.89425	2.14	2.1375
	1	3.35928	-0.45363	2.58	2.57812
	2		-0.26188		2.76987
2	0	3.35931	-0.42131	2.61	2.61044
	1		-0.25822		2.77352

TABLE V. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 2. Our replication computation is also shown for comparison. Exciton I_9 with $D = 19.1$ meV.

The replication results for the relative energies agree with those quoted in the paper, within rounding. However, with the exact same code, the replication of the absolute energies are the wrong sign and wrong order of magnitude when compared to those quoted in the paper. One could suspect that an error was made on their part, and shows potentially some typos or mistakes in the paper.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (meV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3598	-2.22736	0	0
	1	3.36132	-0.70743	1.52	1.51993
	2	3.3617	-0.32585	1.9	1.90151
1	0	3.36138	-0.64327	1.58	1.58409
	1	3.36171	-0.32075	1.91	1.90661
	2		-0.18442		2.04294
2	0	3.36173	-0.30071	1.93	1.92665
	1		-0.18224		2.04512

TABLE VI. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 2. Our replication computation is also shown for comparison. Exciton I_8 with $D = 16.0$ meV.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (meV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.36	-2.17868	0	0
	1	3.36149	-0.69036	1.49	1.48832
	2	3.36186	-0.31785	1.86	1.86083
1	0	3.36155	-0.62832	1.55	1.55036
	1	3.36187	-0.31293	1.87	1.86575
	2		-0.17988		1.9988
2	0	3.36189	-0.29357	1.89	1.88511
	1		-0.17778		2.0009

TABLE VII. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 2. Our replication computation is also shown for comparison. Exciton I_7 with $D = 15.8$ meV.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (meV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3608	-1.9881	0	0
	1	3.36212	-0.62404	1.32	1.36405
	2	3.36244	-0.28683	1.64	1.70126
1	0	3.36217	-0.57008	1.37	1.41802
	1	3.36245	-0.2826	1.65	1.70549
	2		-0.16228		1.82582
2	0	3.36246	-0.2658	1.66	1.7223
	1		-0.16047		1.82762

TABLE VIII. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 2. Our replication computation is also shown for comparison. Exciton I_6 with $D = 15.0$ meV.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (meV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3628	-1.54169	0	0
	1	3.36386	-0.47219	1.06	1.0695
	2	3.36411	-0.2161	1.31	1.32559
1	0	3.36389	-0.43554	1.09	1.10615
	1	3.36411	-0.21332	1.31	1.32837
	2		-0.12217		1.41952
2	0	3.36412	-0.20197	1.32	1.33972
	1		-0.12098		1.42071

TABLE IX. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 2. Our replication computation is also shown for comparison. Exciton I_4 with $D = 13.0$ meV.

Table 3 from the Meyer 2010 paper, along with its Eq. 3, were also examined. Their Eq. 3 describes the excited states of donor bound excitons, and is given by,

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$$E = E_g + 2R_D \left[a^2 - \frac{11}{8}a - \frac{s^2 t^2}{2}\sigma^{-1} \left(n_r + \frac{1}{2} + \sqrt{\left(l + \frac{1}{2}\right)^2 + \frac{st^2}{a}\sigma^{-1}} \right)^{-2} \right] \quad . \qquad (27)$$

Note that Meyer has a misprint with respect to the position of the -2 exponent. Here again, s and t are fitted constants, and $a = \frac{a_e}{a_D}$ is the ratio of the Bohr radii of the electrons in the exciton a_e and the donor a_D. The paper claims that this is a variable parameter, yet they keep it constant. $\sigma = \frac{m_e}{m_h}$ where m_h and m_e are the effective masses of the hole and electrons. E_g is the band gap of ZnO and R_D is the variable donor binding energy. n_r and l are the principle and orbital angular momentum quantum numbers respectively. Table X summarizes the fixed parameters used in the verification code.

Physical Parameter	Numerical Value
s	1.10136
t	1.337
a	0.775
m_h	0.59
m_e	0.24
Eg	3.37 eV

TABLE X. The parameters used to verify Eq. 3 in Meyer [4]. Note that the m_e value is different than what was used in the Verlet Algorithm. This value was taken from Meyer's 2004 paper [5].

To verify their numbers, a Python program called 'Meyer2010_Verify_Eq3' was written to compute their Eq. 3. Here, the units were kept in eV, so the R_D values were converted accordingly. The relative and absolute computed energies were consistent with those quoted in the paper. Tables XI - XV show these results and comparisons.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (eV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3567	3.2891	0	0
	1	3.3629	3.2954	6.2	6.2227
	2	3.3697	3.3021	13	12.9343
1	0	3.3696	3.302	12.9	12.8141
	1	3.3723	3.3047	15.6	15.5197
	2		3.3079		18.7443
2	0	3.3754	3.3078	18.7	18.6832
	1		3.3092		20.0946

TABLE XI. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 3. Our replication computation is also shown for comparison. Exciton I_9 with $E_D = 55.8$ meV.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (eV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3598	3.2922	0	0
	1	3.3658	3.2982	6	5.9885
	2	3.3722	3.3046	12.4	12.4475
1	0	3.3721	3.3045	12.3	12.3319
	1	3.36747	3.3071	14.9	14.9356
	2		3.3102		18.0389
2	0	3.3778	3.3102	18	17.9801
	1		3.3115		19.3383

TABLE XII. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 3. Our replication computation is also shown for comparison. Exciton I_8 with $E_D = 53.7$ meV.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (eV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.36	3.2924	0	0
	1	3.366	3.2984	6	5.9717
	2	3.3724	3.3048	12.4	12.4128
1	0	3.3723	3.3047	12.3	12.2974
	1	3.3749	3.3073	14.9	14.8939
	2		3.3104		17.9885
2	0	3.3779	3.3103	17.9	17.9298
	1		3.3117		19.2843

TABLE XIII. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 3. Our replication computation is also shown for comparison. Exciton I_7 with $ED = 53.55$ meV.

nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (eV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3608	3.2932	0	0
	1	3.3667	3.2991	5.9	5.9104
	2	3.3731	3.3055	12.4	12.2853
1	0	3.3729	3.3054	12.1	12.1711
	1	3.3755	3.3079	14.7	14.7409
	2		3.311		17.8037
2	0	3.3785	3.3109	17.7	17.7457
	1		3.3123		19.0862

TABLE XIV. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 3. Our replication computation is also shown for comparison. Exciton I_6 with $E_D = 53.0$ meV.

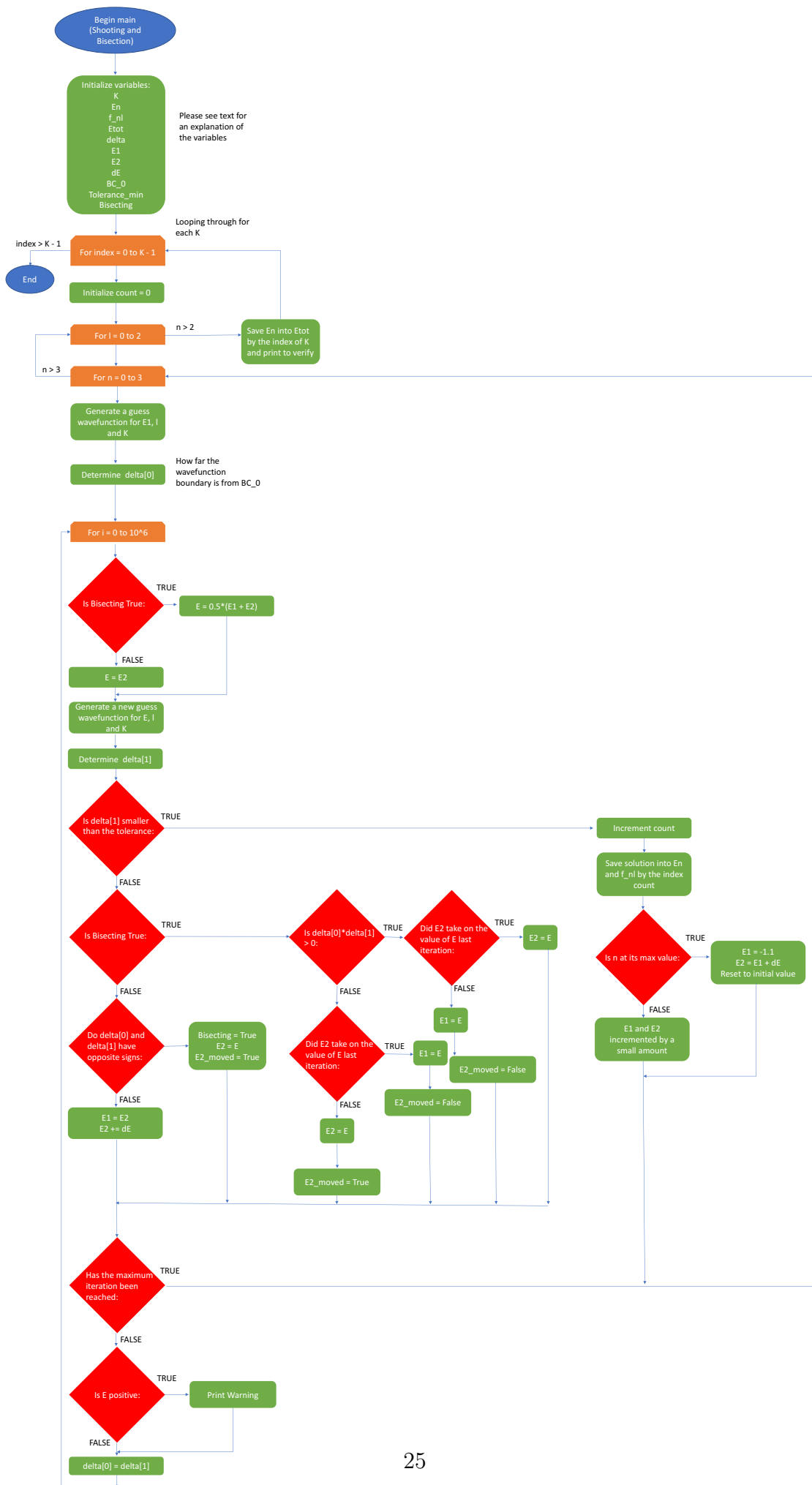| nu	J	Quoted Absolute Excited State Energy (eV)	Replication Absolute Excited State Energy (eV)	Quoted Relative Energy Above Ground State (meV)	Replicated Relative Energy Above Ground State (meV)
0	0	3.3628	3.2952	0	0
	1	3.3686	3.301	5.8	5.7543
	2	3.3748	3.3072	12	11.9608
1	0	3.3747	3.3071	11.9	11.8496
	1	3.3772	3.3096	14.4	14.3516
	2		3.3126		17.3335
2	0	3.3801	3.3125	17.3	17.2769
	1		3.3138		18.5821

TABLE XV. Summary of energies as quoted from the 2010 Meyer paper [4] following its Eq. 3. Our replication computation is also shown for comparison. Exciton I_4 with $D = 51.6$ meV.

In summary, this month we were able to understand, re-write and append to Matthew Frick's eigenvalue solver, and doing so in Python rather than in Julia. We also carefully went through the unit conversions the exciton potentials. We computed energy levels for 12 orbitals, as a function of K and compared our various results (analytical, computational and experimental). The concluded interpretation is not yet clear.

Begin main (Shooting and Bisection)

Initialize variables:
K
En
f_nl
Etot
delta
E1
E2
dE
BC_0
Tolerance_min
Bisecting

Please see text for an explanation of the variables

For index = 0 to K - 1

Looping through for each K

index > K - 1

End

Initialize count = 0

For l = 0 to 2

n > 2

Save En into Etot by the index of K and print to verify

For n = 0 to 3

n > 3

Generate a guess wavefunction for E1, l and K

Determine delta[0]

How far the wavefunction boundary is from BC_0

For i = 0 to 10^6

Is Bisecting True:

TRUE

E = 0.5*(E1 + E2)

FALSE

E = E2

Generate a new guess wavefunction for E, l and K

Determine delta[1]

Is delta[1] smaller than the tolerance:

TRUE

Increment count

Save solution into En and f_nl by the index count

Is n at its max value:

TRUE

E1 = -1.1
E2 = E1 + dE
Reset to initial value

FALSE

E1 and E2 incremented by a small amount

FALSE

Is Bisecting True:

TRUE

Is delta[0]*delta[1] > 0:

TRUE

Did E2 take on the value of E last iteration:

TRUE

E2 = E

FALSE

E1 = E

E2_moved = False

FALSE

Did E2 take on the value of E last iteration:

TRUE

E1 = E

E2_moved = False

FALSE

E2 = E

E2_moved = True

FALSE

Do delta[0] and delta[1] have opposite signs:

Bisecting = True
E2 = E
E2_moved = True

E2_moved = False

FALSE

E1 = E2
E2 += dE

Has the maximum iteration been reached:

TRUE

FALSE

Is E positive:

TRUE

Print Warning

FALSE

delta[0] = delta[1]

25

[1] https://www.feynmanlectures.caltech.edu/III_19.html

[2] Matthew Frick's Report: PulsPaperSummary_ChangesInRed-SW-comments.pdf

[3] J. Puls, F. Henneberger, and J. Voight. Excited states of bound excitons in wurtzite-type semiconductors. phys. stat. sol. (b), 119:291, 1983.

[4] B. K. Meyer, J. Sann, S. Eisermann, and S. Lautenschlaeger. Excited state properties of donor bound excitons in ZnO. phys. rev. B, 115207, 2010.

[5] B. K. Meyer et al. Bound exciton and donor-acceptor pair recombinations in ZnO. phys. stat. sol. (b), 231-260, 2004.