

```

1 begin
2     using Pkg
3     Pkg.activate("../")
4     using Symbolics, LinearAlgebra, Plots
5 end

```

Activating project at `~/projects/AMAT5996`



Problem 1

In this problem we will see how to implement the algorithm mentioned in the paper: [A Tutorial on Matrix Perturbation Theory](#). Notations will follow the paper. We use `Symbolics.jl` to help us document solving process. Let's first define the variables we will use.

```

1 begin
2     @variables E1 E2 a_r a_i b_r b_i λ;
3     a = a_r + im * a_i;
4     b = b_r + im * b_i;
5     nothing
6 end

```

Our Hamiltonian could be divided into two parts. A_0 represents the Hamiltonian before perturbation. A_1 represents the perturbation.

$$\begin{bmatrix} E_1 & 0 & a_r + a_i i \\ 0 & E_1 & b_r + b_i i \\ a_r + (-a_i)i & b_r + (-b_i)i & E_2 \end{bmatrix}$$

```

1 begin
2     A0 = Matrix([E1 0 0; 0 E1 0; 0 0 E2])
3     A1 = Matrix([0 0 a; 0 0 b; conj(a) conj(b) 0])
4     Ae = A0 + A1
5 end
6

```

Let's first try to solve the eigenvalues exactly. We will use `det` to get the characteristic equation. Then we notice that E_1 is a root of this equation. We then divide $\lambda - E_1$ from the equation to get a lower order polynomial which could be solved by quadratic formula.

`chara_eqn =`

$$(E_1 - \lambda) ((E_1 - \lambda)(E_2 - \lambda) - b_i^2 - b_r^2) - a_i^2 (E_1 - \lambda) - a_r^2 (E_1 - \lambda)$$

```

1 chara_eqn = det(Ae - λ .* Matrix(I, 3, 3))

```

0

```
1 substitute(chara_eqn, Dict(λ => E1))
```

reduced_chara_eqn =

$$E_1 E_2 - E_1 \lambda - E_2 \lambda - a_i^2 - a_r^2 - b_i^2 - b_r^2 + \lambda^2$$

```
1 reduced_chara_eqn = -1 * simplify(chara_eqn / (λ - E1))
```

```
1 begin
2   const_term = substitute(reduced_chara_eqn, Dict(λ => 0))
3   linear_term = substitute(simplify((reduced_chara_eqn - const_term) / λ), Dict(λ
=> 0))
4   quadratic_term = simplify((reduced_chara_eqn - const_term - linear_term * λ) /
λ^2)
5   nothing
6 end
```

```
1 b2m4ac = real(simplify(linear_term^2 - 4 * quadratic_term * const_term))
```

```
1 root2 = simplify((-linear_term + sqrt(b2m4ac)) / (2 * quadratic_term))
```

```
1 root3 = simplify((-linear_term - sqrt(b2m4ac)) / (2 * quadratic_term))
```

In summary, we have the following three eigenvalues of the perturbed Hamiltonian.

$$1. \quad \lambda_1 = E_1$$

$$2. \quad \lambda_2 = \frac{1}{2} \left(E_1 + E_2 + \sqrt{(E_1 - E_2)^2 + 4(a_i^2 + a_r^2 + b_i^2 + b_r^2)} \right)$$

$$3. \quad \lambda_3 = \frac{1}{2} \left(E_1 + E_2 - \sqrt{(E_1 - E_2)^2 + 4(a_i^2 + a_r^2 + b_i^2 + b_r^2)} \right)$$

Note, we could apply the approximation $\sqrt{1+x} \approx 1 + x/2$ when $x \ll 1$. And get

$$1. \quad \lambda_1 = E_1$$

$$2. \quad \lambda_2 \approx \left(E_1 - \frac{(a_i^2 + a_r^2 + b_i^2 + b_r^2)}{(E_2 - E_1)} \right)$$

$$3. \quad \lambda_3 \approx \left(E_2 + \frac{(a_i^2 + a_r^2 + b_i^2 + b_r^2)}{(E_2 - E_1)} \right)$$

Let's try to solve for the eigenvalues using perturbation approach. Firstly, let's blindly apply the non-degenerate perturbation method to second order. Let's do first order perturbation. We know the Hamiltonian before perturbation has eigenvalues E_1, E_1, E_2 and eigenvectors $[1, 0, 0]$, $[0, 1, 0]$, $[0, 0, 1]$ respectively.

```
1 A0
```

We can define V_0 and Λ_0 accordingly.

```
1 V0 = Matrix([1 0 0; 0 1 0; 0 0 1])
```

```
1 Λ0 = diagm([E1,E1,E2])
```

We could use eqn (11) from Bamieh to get first order perturbation to eigenvalues.

$$\Lambda_1 = dg(V_0^* A_1 V_0)$$

```
1 Λ1 = Diagonal(V0' * A1 * V0)
```

```
2
```

Unfortunately, we get nothing from the first order perturbation. Let's go to the next level where we also allow the eigenstate to vary a little.

```
1 Πdagcirc = Matrix([0 0 1/(E1-E2); 0 0 1/(E1-E2); 1/(E2-E1) 1/(E2-E1) 0])
```

```
1 V1 = -V0 * (Πdagcirc .* (V0 * A1 * V0))
```

```
2
```

```
1 Λ2 = simplify.(Diagonal(V0 * A1 * V1))
```

Comparing this to our exact result above, we can see something is wrong. For correction of first and second eigenstate, we got it wrong. The energy correction term should be

$$1. \quad \delta\lambda_1 = 0$$

$$2. \quad \delta\lambda_2 = -\frac{(a_i^2 + a_r^2 + b_i^2 + b_r^2)}{(E_2 - E_1)}$$

$$3. \quad \delta\lambda_3 = \frac{(a_i^2 + a_r^2 + b_i^2 + b_r^2)}{(E_2 - E_1)}$$

Let's try to apply degenerate energy perturbation theory. We notice for vector spanned by $\{[1 \ 0 \ 0], [0 \ 1 \ 0]\}$, we have energy degeneracy for Λ_0 .

According to the paper, we need to find a special pair of linear combinations of the above mentioned basis vectors so that we diagonalize A_1 in this subspace. However, we could not as A_1 is already diagonalized and degenerate.

```
1 A1[1:2,1:2]
```

In this case, the paper does not tell us what to do. I found [Gottfried Chapter 3.7](#) to be extremely helpful. Using (273) directly gives us the effective Hamiltonian of a lower dimension (the dimension of degenerate subspace). Reading off the (272) you could immediately see that the eigenvalue of this effective hamiltonian is the energy change from original Hamiltonian.

```
1 Heff = Matrix(simplify.([ A1[i,3]*A1[3,j]/(E1 - E2) for i in 1:2, j in 1:2 ]))
```

```
1 simplify(det(Heff - λ * Matrix(I,2,2)))
```

It's obvious that one solution is $\lambda = 0$ and the other is $\lambda = \frac{|a|^2 + |b|^2}{E_2 - E_1}$ This matches our exact calculation above.

Problem 2: Scaling Laws for Hydrogen-like Atoms

I found the following [lecture](#) and [lecture note](#). helpful when preparing this solution. We will largely follow it hence taking a semi-classical approach. This should be enough since we are only interested in the scaling laws.

Recall a hydrogenlike atom is defined as a cation or an atom with only one valence shell electron. Since we only have one valence electron, we have a nice spherical symmetry. Due to the spherical symmetry of the system, we could separate the wavefunction of the valence electron into a radial part and an angular part. The angular part will be no different from the angular part of a hydrogen atom. It's the radial part that we need to solve.

Firstly, we need to adjust the potential energy term to account for the nuclear charge and angular momentum of the valence electron (think about merry-go-around). This gives us the following potential

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2m_e r^2}$$

where Z is the nuclear charge, e is the elementary charge, ϵ_0 is the vacuum permittivity, l is the angular momentum quantum number, \hbar is the reduced Planck constant, and m_e is the mass of the electron.

Solving the Schrodinger Equation with this potential is a bit tedious. We will not do it here. It's largely similar to the process given in Griffiths' book. I have uploaded the relevant part in [zulip](#).

For the sake of obtaining a scaling law, we resort back to the Bohr model. For details of derivation, please refer to [Libre Text](#). I jump to conclusion directly.

```
1 @variables n;
```

```

1 function E_scaling(n::Num)
2     return -1/n^2
3 end

```

```

1 function ΔE_scaling(n::Num)
2     return simplify(E_scaling(n+1) - E_scaling(n))
3 end

```

```

1 function r_scaling(n::Num)
2     return n^2
3 end

```

```

1 # ~ 1/n^3
2 ΔE_scaling(n)

```

Let's pause for a moment and think about the physical meaning of the scaling laws we just derived. The energy scaling is helpful when we want to know the energy level which the electron in the atom is in given the ionization energy.

To estimate the rest of the quantities, we need to rely on the trick to estimate the integral of two radial part of the wavefunction mentioned in the video lecture.

For dipole polarizability, we use the formula provided in [paper](#) and our previous estimation of Transition dipole moment for adjacent states and energy splitting to get

$$\alpha \sim \frac{(n^2)^2}{n^{-3}} = n^7$$

van der Waal's interaction coefficient???