

Quantum Computing for Quantum Chemistry - Exercises

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1 Lecture 1

1. Considering the energy levels of atomic orbitals in each valence shell shown in figure 1, and using a periodic table:

(a) Write the electron configurations for the following atoms and ions:

- i Ne,
- ii Ar^+ ,
- iii C,
- iv O,
- v (optional) Br^- .

Hint: For Mg, the electron configuration is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2$, or $1s^2 2s^2 2p^6 3s^2$ since the p shell is fully occupied. Aufbau principle dictates that the lowest energy atomic orbitals are filled first.

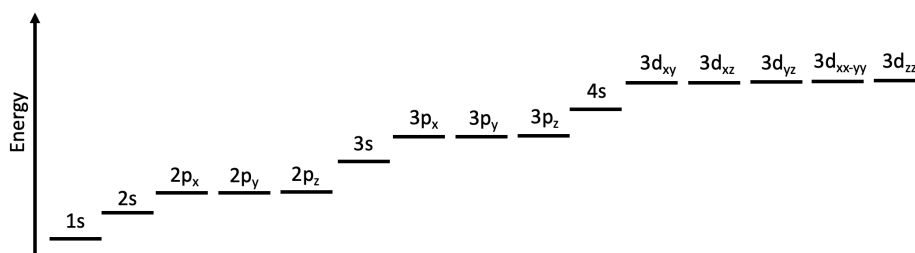


Figure 1: Atomic orbital energy levels.

- (b) For the following systems, construct molecular orbital diagrams:

- i. Hydrogen Fluoride (HF)
- ii. (optional) Water (H_2O)

Hint: Not all molecular orbitals are bonding orbitals! The heavier an atom, the lower the energy of the core electrons, so they are often

bystanders in bonding interactions. The number of molecular orbitals must be equal to the number of atomic orbitals. For part (ii) first think about how you can combine the two H 1s orbitals, and place those combinations on one side of your MO diagram.

- (c) The ground-state wavefunction of the Hydrogen atom is given by,

$$\psi_{1,0,0} = \left(\frac{\xi^3}{\pi}\right)^{\frac{1}{2}} e^{-\xi r}. \quad (1)$$

Since this is an isolated, one-electron system, we only need to consider electronic kinetic energy and nucleus-electron attraction. The kinetic energy operator is the radial Laplacian,

$$\hat{T} = -\frac{1}{2r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right). \quad (2)$$

The potential energy operator for a hydrogen-like system is,

$$\hat{V} = -\frac{Z}{r}. \quad (3)$$

The expectation values of each operator \hat{T} and \hat{V} with respect to ψ are given by

$$\langle \hat{T} \rangle = \frac{\xi^2}{2m} \quad (4)$$

and

$$\langle \hat{V} \rangle = -\xi Z, \quad (5)$$

respectively, where m is the electron mass and Z is the charge of the nucleus. The total energy is,

$$E = \frac{\xi^2}{2m} - \xi Z. \quad (6)$$

For the **Hydrogen atom**:

- i. Use this information to find the optimum value of ξ . That is, the value which gives the lowest total energy.

Hint: In atomic units $m = 1$ and $Z = 1$. Full description in Szabo & Ostlund (chapter 2).

- ii. Plot the kinetic, potential and total energies as functions of ξ on the same graph.
- iii. (optional) Add to your plot from (ii), one side of the virial equation ($-V/2$). Where does this intersect with the kinetic energy? Is this consistent with the value determined for ξ in part (i) of this question?

- iv. Inspect figure 2 and, with the information from part (ii) of this question, arrive at your own conclusions for the origin of the bond in H_2^+ . How is the molecular orbital expanding and contracting throughout the formation of the bond?

Hint: Begin at large internuclear separation, the bond is at its strongest at $2a_0$.

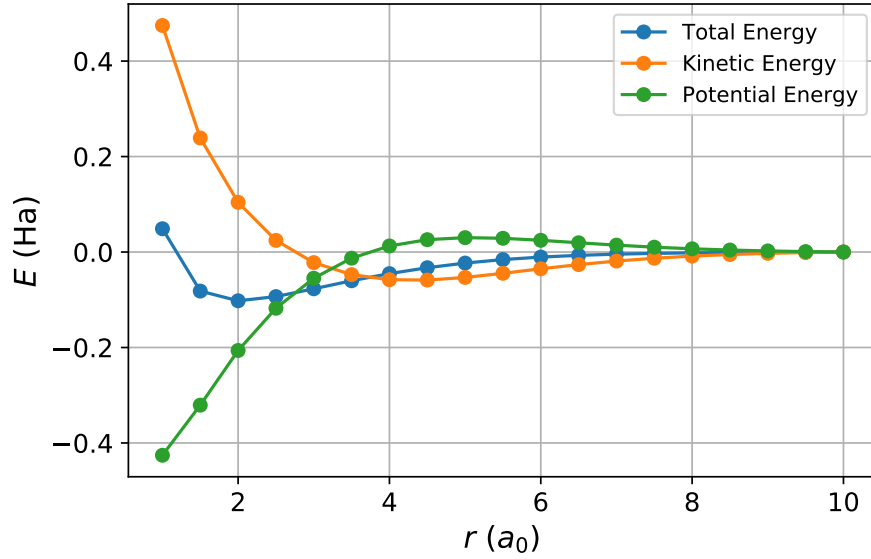


Figure 2: The total (blue line), kinetic (orange line) and potential (green line) energy against nuclear separation for H_2^+ , minus the asymptotic values.

2. Given that the 2s (2, 0, 0) hydrogen atom solution is described by

$$\psi_{2,0,0} = \frac{1}{4\sqrt{2\pi}a_0^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}. \quad (7)$$

Using the Born rule $|\langle\psi(r)|\psi(r)\rangle|^2 = \rho(r)$ for probability density, with sympy.plotting draw the radial distribution functions for the 1s and 2s solutions.

3. For the Shrodinger equation governing the particle in a box. For the general solution

$$\psi(x) = C \sin(kx) + D \cos(kx) \quad (8)$$

and the boundary conditions

$$\psi(0) = 0 = C \sin(0) + D \cos(0) = D \quad (9)$$

and $D = 0$. At $x = L$,

$$\psi(L) = 0 = C \sin(kL) \quad (10)$$

show that the energy is quantized by

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad (11)$$

4. The general solution to the Hydrogen atom is given by:

$$\psi_{n\ell m}(r, \theta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right) Y_\ell^m(\theta, \varphi) \quad (12)$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e q^2}$ is the Bohr radius, $L_{n-\ell-1}^{2\ell+1}(\dots)$ are the generalized Laguerre polynomials of degree $n - \ell - 1$ given by

$$L_n^{(\alpha)}(x) = \frac{x^{-\alpha} e^x}{n!} \frac{d^n}{dx^n} (e^{-x} x^{n+\alpha}) = \frac{x^{-\alpha}}{n!} \left(\frac{d}{dx} - 1\right)^n x^{n+\alpha}. \quad (13)$$

$Y_\ell^m(\theta, \varphi)$ are the spherical harmonics given by

$$Y_\ell^m(\theta, \varphi) = (-1)^m \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}} P_\ell^m(\cos\theta) e^{im\varphi} \quad (14)$$

n, ℓ, m are the principal quantum number, azimuthal quantum number, and magnetic quantum number, respectively, which take the values $n = 1, 2, 3, \dots$, $\ell = 0, 1, 2, \dots, n-1$, $m = -\ell, \dots, \ell$.

- (a) Using numpy or sympy (or both), plot all the f orbitals in at a suitable radius using the born rule $|\langle\psi(r)|\psi(r)\rangle|^2 = \rho(r)$. Where the edge of the isosphere is some arbitrary probability density.

Hint: <https://www.cfm.brown.edu/people/dobrush/am33/SymPy/part1.html> or https://matplotlib.org/stable/gallery/mplot3d/surface3d_radial.html

- (b) Plot a g orbital, why has this not been observed in matter.

- (c) Where would an atom with a g valence electron go in the periodic table.

5. Calculate the ground state energy of the $p = (2, 1, 0)$ orbital

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{Z\mathbf{r}}{a_0} e^{-\frac{Z\mathbf{r}}{2a_0}} \cos\theta \quad (15)$$

,

Given the Hamiltonian operator for the stationary hydrogen atom

$$\hat{H} = -\frac{1}{m_1 \mathbf{r}^2} \left\{ \frac{\partial}{\partial \mathbf{r}} \left(\mathbf{r}^2 \frac{\partial}{\partial \mathbf{r}} \right) - \frac{1}{\sin^2 \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right] \right\} - \frac{1}{r}, \quad (16)$$

and the energy of an operator acting on a given state is given by

$$E = \int \psi^*(\mathbf{r}, \theta, \phi) \hat{H} \psi(\mathbf{r}, \theta, \phi) d\mathbf{r} d\theta d\phi \quad (17)$$

If this is too hard to do by hand try using a numerical integral solver.

6. Using the linear combination of atomic orbitals. Find the energy of the bonding and anitbonding orbital in H2 a $1s - 1s$ σ bond. Where the energy is given by the secular equation. (This can be done by hand or on a computer.)

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = E \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} \quad (18)$$

With the Hamiltonian elements given by:

$$\begin{aligned} H_{AA} &= \int d\mathbf{r} s_A^*(\mathbf{r}) H_{LCAO} s_A(\mathbf{r}) \\ &= \int d\mathbf{r} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \left[\nabla_A^2 + \frac{1}{|r - R_A|} + \frac{1}{|r - R_B|} \right] \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \end{aligned} \quad (19)$$

and the overlap elements

$$\begin{aligned} S_{AA} &= \int d\mathbf{r} s_A^*(\mathbf{r}) s_A(\mathbf{r}) \\ &= \int d\mathbf{r} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \end{aligned} \quad (20)$$

2 Lecture 2

1. Show that in the Hartree Fock approximation electrons with opposite spins in He molecule are correctly correlated and cannot occupy the same point in space.

$$|\chi_1\chi_2\rangle = \frac{1}{\sqrt{2}}(\phi_1(\mathbf{r}_1)\alpha(\sigma_1)\phi_2(\mathbf{r}_2)\alpha(\sigma_2) - \phi_2(\mathbf{r}_1)\alpha(\sigma_1)\phi_1(\mathbf{r}_2)\alpha(\sigma_2)) \quad (21)$$

Hint: Use the properties of spin

Where does this correct treatment of correlation arise from?

2. The variational principle states that the expectation value of an approximate ground state (i.e. an ansatz state) with the Hamiltonian is always higher than the true ground-state energy, such that

$$\langle\psi_a|H|\psi_a\rangle \geq E_g \quad (22)$$

where $|\psi_a\rangle$ is the ansatz state, H is the Hamiltonian and E_g is the ground state energy.

- (a) Can this principle be justified through physical intuition?
 - (b) How can this principle be used computationally?
 - (c) Can this principle be proved mathematically? (Hint: decompose $|\psi_a\rangle$ in the eigenbasis of the Hamiltonian.)
 - (d) If the relation (22) is an exact equality, what does it imply about $|\psi_a\rangle$?
3. Using the quantum chemistry package PySCF, generate a plot of ground state energy vs. bond length for the H_2 molecule using the Hartree-Fock method and the 'sto-3g' basis set. (See attached jupyter notebook with more instructions)
 - (a) What happens when you use a different basis set - for instance, the 'cc-pvdz-pp' basis set? Try putting both curves on the same graph. What are the differences between the curves? What could explain the differences? Which do you think better describes the "true" ground state of the molecule?
 - (b) Are there any disadvantages to using the better basis set? (Hint: slap a timer on it)
 - (c) Try plotting the energy using Full Configuration Interaction (FCI) instead of Hartree-Fock (instructions to get PySCF to run FCI are in the notebook).
 - (d) Put the Hartree-Fock 'STO-3G' curve and the FCI 'STO-3G' curve on the same graph. How do these curves differ? What might this suggest about the Hartree-Fock method?

- (e) Are there any disadvantages to using the "better" method? (Hint: time it. Also try putting a big molecule in if you want to see what an exploding laptop looks like.)
4. For the wavefunction $\psi(\mathbf{x}) = c_1\phi_1(\mathbf{x}) + c_2\phi_2(\mathbf{x})$. Where the basis is $\int \phi_1(\mathbf{x})\phi_2(\mathbf{x}) = 0$.
- (a) What does $\int \phi_1(\mathbf{x})\phi_2(\mathbf{x}) = 0$ signify
- (b) Evaluate:

$$\frac{\partial}{\partial c_n} \int \psi^*(\mathbf{x}) \hat{H} \psi(\mathbf{x}) d\mathbf{x} = 0 \quad (23)$$

What satisfies the $= 0$ condition?

- (c) Find the general form of equation 23 when $\psi(\mathbf{x}) = \sum_n c_n \phi_n(\mathbf{x})$ when ψ is orthogonal.
- (d) Physically what does this condition being satisfied represent
- (e) From this expression derive the Secular equation for an orthogonal basis

$$\mathbf{H}\mathbf{c} - E\mathbf{c} = 0 \quad (24)$$

- (f) Find the general form of equation 23 when $\psi(\mathbf{x}) = \sum_n c_n \phi_n(\mathbf{x})$ when ψ is not orthogonal.
- (g) From this expression derive the Secular equation for a non-orthogonal basis

$$\mathbf{H}\mathbf{c} - E\mathbf{S}\mathbf{c} = 0 \quad (25)$$

5. Derive the variational principle for excited states.

3 Lecture 3

1. In second quantization, operators (such as the Hamiltonian) are described by sequences of creation and annihilation operators, acting on orbitals.

$$\begin{aligned} a_i^\dagger |0\rangle_i &= |1\rangle_i & a_i |0\rangle_i &= 0 \\ a_i^\dagger |1\rangle_i &= 0 & a_i |1\rangle_i &= |1\rangle_i \end{aligned} \quad (26)$$

Here, $|0\rangle$ is an *unoccupied* mode (it doesn't have a particle in it) and $|1\rangle$ is an *occupied* mode (it has a particle in it). By definition, for fermions, the creation and annihilation operators have the anticommutation relations:

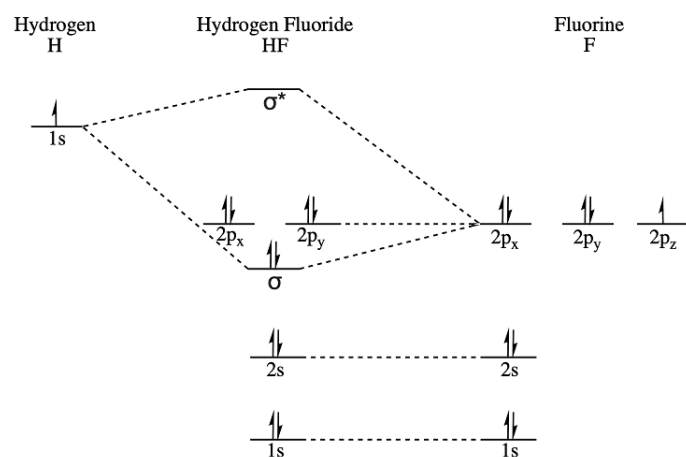
$$\begin{aligned} \{a_i^\dagger, a_j\} &= \delta_{i,j} \\ \{a_i^\dagger, a_j^\dagger\} &= 0 \\ \{a_i, a_j\} &= 0 \end{aligned} \quad (27)$$

- (a) Using eqns. (26), derive an operator \hat{O} composed of creation and annihilation operators which counts the number of fermions in the system – i.e. $\langle 0010 | \hat{O} | 0010 \rangle = 1$, $\langle 11011 | \hat{O} | 11011 \rangle = 4$ and so on. (Hint: start with the case with only one fermionic mode)
- (b) Using the result of the previous question, derive an operator \hat{P} composed of creation and annihilation operators which applies a -1 phase to a state if the number of fermions is odd, and leaves the state unchanged if the number of fermions is even – i.e. $\hat{P} | 0010 \rangle = - | 0010 \rangle$, $\hat{P} | 11011 \rangle = | 11011 \rangle$ and so on. (Hint: also start with the 1 mode case. How would combining these single-mode operators be different from the previous question?)
- (c) Ignore the anticommutation relations (eqns (27)) for now. Just looking at eqns (26), find a linear combination of Pauli operators which would implement the same operation as a_i^\dagger and a_i^\dagger on a qubit. Can we make a circuit to implement this operator? Now considering eqns (27), show that we cannot use these qubit operators to simulate fermions.
- (d) Extremely difficult, probably do the rest of the sheet first: based on the fermionic and qubit operators generated in the previous questions, generate qubit operators which *can* be used to simulate fermions.

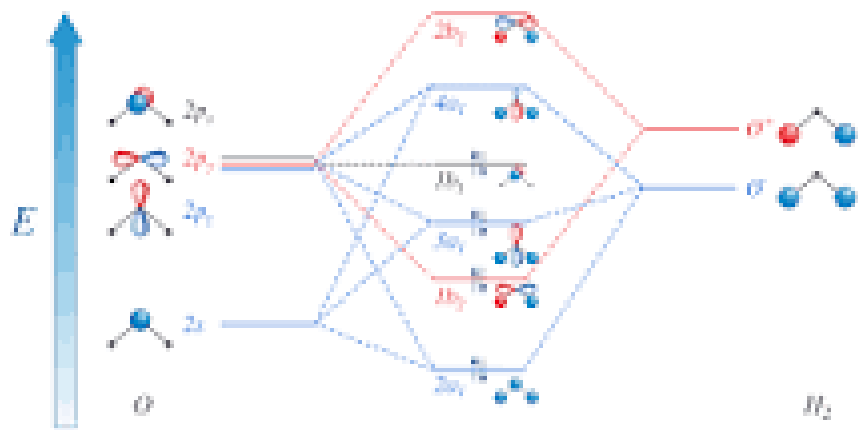
4 Lecture 4

Lecture 1 – Solutions

- 1(a) i $1s^2 2s^2 2p^6$
 ii $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
 iii $1s^2 2s^2 2p_x^1 2p_y^1$
 iv $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
 v $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p_x^2 4p_y^2 4p_z^2$



- 1(b) i



- ii

2. (a) Substitute $m = 1$, $Z = 1$ into expression for E , differentiate w/respect

to ξ , solve for ξ .

$$E = \frac{\xi^2}{2} - \xi \quad (28)$$

$$\frac{\partial E}{\partial \xi} = \xi - 1 = 0 \quad (29)$$

$$\xi = 1 \quad (30)$$

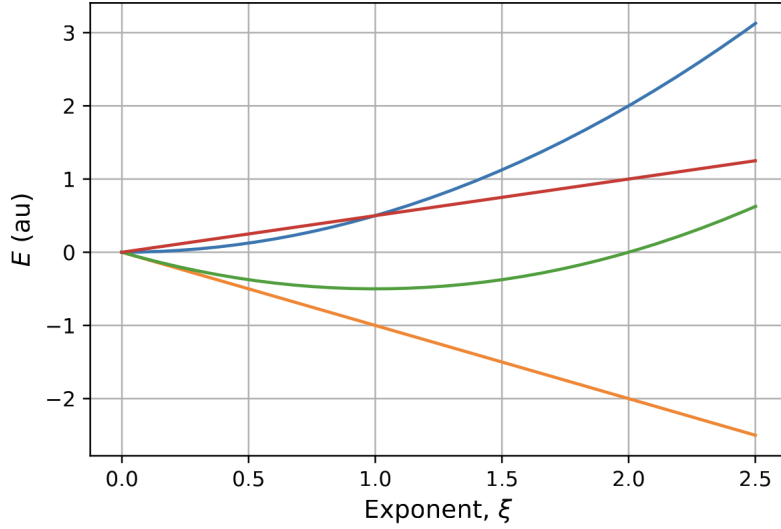


Figure 3: The kinetic (blue), potential (orange) and total (green) energies of the H atom as a function of orbital exponent. The red line is $-V/2$ where V is the potential energy.

- (b)
- (c) Intersect is at 1.0, matches exponent. Only nonzero intersect obtained at minimum and when virial theorem satisfied. Virial theorem only satisfied at energetic minimum.
- (d) Starting from asymptotic separation, no change until about 7.75 bohr. When atomic orbitals start to overlap potential energy goes **up**, not down, contrary to what most undergraduate textbooks say. Kinetic energy goes down. Inspection of plot from part (b/c) shows that kinetic energy goes down when wavefunction more diffuse, electron can occupy more space without tunneling. Kinetic energy therefore responsible for driving bond formation. Once within close proximity, orbital contracts, less space for electron to occupy, kinetic energy goes up. Electron “closer” to nucleus, potential energy goes down. Potential energy takes over driving bond formation once it has already been initiated.

Lecture 2 – Solutions

- 1.
2. (a) Yes. Nature will find the optimal solution. If your ansatz state was within the relevant Hilbert space and had *lower* energy than the ground state, then this itself would have to be the ground state. Hence, the ground state energy must be the lowest energy state in the full Hilbert space, so our ansatz can only ever be higher.
- (b) We can use it to guide optimisation to find a good approximation to the true ground state – the lower our energy goes, the "better" our ansatz state.
- (c) We decompose our ansatz state in the eigenbasis of the Hamiltonian:

$$|\psi\rangle_a = \sum_i c_i |\phi\rangle_i \quad (31)$$

then

$$\langle\psi|_a H |\psi\rangle_a = \sum_i \sum_j c_i^* c_j \langle\phi|_i H |\phi\rangle_j \quad (32)$$

$|\phi\rangle$ are eigenvectors of the Hamiltonian, so:

$$\langle\psi|_a H |\psi\rangle_a = \sum_i \sum_j c_i^* c_j E_j \langle\phi|_i |\phi\rangle_j \quad (33)$$

$|\phi\rangle_i$ and $|\phi\rangle_j$ are orthonormal:

$$\langle\psi|_a H |\psi\rangle_a = \sum_i |c_i|^2 E_i \quad (34)$$

E_0 is the ground state energy and $|c_i|^2$ is always positive, so the minimum this can be is E_0 (when $c_0 = 1$ and other $c_i = 0$). Thus:

$$\langle\psi|_a H |\psi\rangle_a \geq E_0 \quad (35)$$

- (d) $|\psi\rangle_a$ is the exact ground state (or in the ground subspace).
3. (a) We start with the case of one mode. First we notice that just applying a distinguishes the $|0\rangle$ and $|1\rangle$ - for $|0\rangle$ it will obliterate the state entirely, whereas for $|1\rangle$ it just changes it to $|0\rangle$. In the first case, operating on the "state" (now zero) with anything will always give zero. So we can 1) operate on the state with a , then 2) operate on the state with the operator that takes $|0\rangle$ to $|1\rangle$. From eqn (27), we see that the operator that does 2) is a^\dagger . So the answer for one mode is $a^\dagger a$. (This is a "number operator"). To get the multi-mode case, we can just add them up - by linearity, we will get the desired expectation value. So we have $\sum_i a_i^\dagger a_i$
- (b) For the single mode case, we know that $a^\dagger a |0\rangle = 0$ and $a^\dagger a |1\rangle = |1\rangle$. From this, we can spot that we could get the desired phase by doing $I - 2a^\dagger a$ ($1 - 0 = 1, 1 - 2 = -1$). In contrast to the previous

question, here we notice that we have to take the product to get the multi-mode result (consider $-1 * 1 * 1 * -1 \dots$ vs $-1 + 1 + 1 - 1$), so we have $\prod_i (I - 2a_i^\dagger a_i)$. Note that this is equivalent to $(-1)^{\sum_i a_i^\dagger a_i}$

- (c) $a^\dagger \rightarrow X - iY, a \rightarrow X + iY$ (this might be a "just have to spot it" type of question unfortunately, but one could go via generating a matrix representation). We can't make a circuit for this - it's not unitary. To show it doesn't work as a way to simulate fermions, plug $a^\dagger \rightarrow X - iY, a \rightarrow X + iY$ into a_i^\dagger, a_j . After some algebra we get $2X_i X_j + 2Y_i Y_j$, which is not $\delta_{i,j}$. So this substitution does not replicate the fermionic anticommutation relations.
- (d) https://en.wikipedia.org/wiki/Jordan-Wigner_transformation