21. Consider a triatomic molecule with three identical atoms that are bound together with each atom at its own corner of an equilateral triangle of edge length $a$. An electron added to the molecule (to form a molecular ion) can be put in an identical atomic orbital on any one of the three atoms. Denote the atomic states in which the electron is on atom $i$ as $|i\rangle$, and assume that these three states $\{i\}$, $|1\rangle$, $|2\rangle$, and $|3\rangle$, form an orthonormal set. Set the zero of potential energy so that the mean energy associated with each such state vanishes, i.e., $\langle i|H|i\rangle = 0$ for each state $|i\rangle$. Suppose also that the electron on an atom can move to either of its neighbors, such that

$$\langle i|H|j\rangle = V_0 \quad i \neq j$$

(a) Construct a $3 \times 3$ matrix $[H]$ that represents the Hamiltonian within the subspace spanned by these 3 atomic states, using the states $\{i\}$ as an ONB for the subspace. Find the trace of this matrix. From the information given it is clear that

$$[H] = \begin{pmatrix}
0 & V_0 & V_0 \\
V_0 & 0 & V_0 \\
V_0 & V_0 & 0
\end{pmatrix}$$

(b) Find the energy eigenvalues and the degeneracies of this molecular ion. The characteristic equation $\det ([H] - \epsilon I) = 0$ can be written

$$\begin{vmatrix}
-\epsilon & V_0 & V_0 \\
V_0 & -\epsilon & V_0 \\
V_0 & V_0 & -\epsilon
\end{vmatrix} = -\epsilon^3 + 3\epsilon V_0^2 + 2V_0^3 = 0.$$ 

This third order polynomial easily factors, giving the equivalent equation $(\epsilon - 2V_0)(\epsilon + V_0)^2 = 0$, from which we determine that there are two distinct eigenvalues

$$\epsilon_0 = -V_0 \quad n_0 = 2$$

which is two fold degenerate, and

$$\epsilon_1 = 2V_0 \quad n_1 = 1$$

which is non-degenerate.

(c) Construct an ONB of eigenstates $\{|\epsilon_n, \tau\rangle\}$ of the system, as linear combinations of the atomic states. (The $\tau$ is included in the notation to allow for degenerate eigenvalues.) The two-fold degenerate ground state has eigenstates $|\chi\rangle = \sum \chi_i |i\rangle$ that satisfy

$$\begin{pmatrix}
V_0 & V_0 & V_0 \\
V_0 & V_0 & V_0 \\
V_0 & V_0 & V_0
\end{pmatrix} \begin{pmatrix}
\chi_1 \\
\chi_2 \\
\chi_3
\end{pmatrix} = \begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix}$$

Although this gives three linear equations, only one is linearly independent (i.e., $N - n_0 = 3 - 2 = 1$). The first row gives $\chi_1 + \chi_2 + \chi_3$. Taking $\chi_1 = 0$ and $\chi_2 = -\chi_3 = 1$ gives one un-normalized solution $|\chi\rangle = |2\rangle - |3\rangle$, which normalization turns into

$$|\epsilon_0, 1\rangle = \frac{1}{\sqrt{2}} (|2\rangle - |3\rangle)$$

taking $\chi_1 = 2$ and $\chi_2 = \chi_3 = -1$ gives another, i.e., $|\chi\rangle = 2|1\rangle - |2\rangle - |3\rangle$, which is easily verified to be orthogonal to $|\epsilon_0, 1\rangle$. If it were not, one could use the Graham-Schmidt procedure to subtract off part of $|\chi\rangle$ lying along $|\epsilon_0, 1\rangle$ and then normalize. After normalization we obtain the vector

$$|\epsilon_0, 2\rangle = \frac{1}{\sqrt{6}} (2|1\rangle - |2\rangle - |3\rangle)$$
Other choices are, of course possible in this two-dimensional eigenspace. The non-degenerate eigenvalue has an eigenstate that satisfies
\[
\begin{bmatrix}
-2V_0 & V_0 & V_0 \\
V_0 & -2V_0 & V_0 \\
V_0 & V_0 & -2V_0
\end{bmatrix}
\begin{bmatrix}
\chi_1 \\
\chi_2 \\
\chi_3
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\]
\[
\begin{bmatrix}
-2V_0 & V_0 & V_0 \\
V_0 & -2V_0 & V_0 \\
V_0 & V_0 & -2V_0
\end{bmatrix}
\begin{bmatrix}
1 \\
-1 \\
3
\end{bmatrix}
= \begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
\]
which will generate two linearly independent equations. From the first row we find that
\[
2\chi_1 = \chi_2 + \chi_3
\]
and from the second, we find
\[
2\chi_2 = \chi_1 + \chi_3
\]
Solving these gives \( \chi_1 = \chi_2 = \chi_3 \). Normalization gives the non-degenerate energy eigenvector
\[
|\varepsilon_1\rangle = \frac{1}{\sqrt{3}} \left[ |1\rangle + |2\rangle + |3\rangle \right].
\]
Thus our basis of energy eigenstates is
\[
|\varepsilon_0, 1\rangle = \frac{1}{\sqrt{2}} \left[ |2\rangle - |3\rangle \right]
\]
\[
|\varepsilon_0, 2\rangle = \frac{1}{\sqrt{6}} \left[ 2|1\rangle - |2\rangle - |3\rangle \right]
\]
\[
|\varepsilon_1\rangle = \frac{1}{\sqrt{3}} \left[ |1\rangle + |2\rangle + |3\rangle \right]
\]
22. Let \{ |n\rangle \}, with \( n = 0, 1, 2, \ldots \), be a discrete ONB for a quantum state space \( S \). Let \( A \) be an operator such that \( \langle n | A = \langle n + 1 | \), for all \( n = 0, 1, 2, \ldots \).

(a) Find matrix elements of \( A \) and \( A^+ \) in this representation. Show that \( A|0\rangle = 0 \).

We find that
\[
\langle n | A | n' \rangle = \langle n + 1 | n' \rangle = \delta_{n', n+1}
\]

Taking the adjoint of this last expression and switching primed and unprimed indices gives
\[
\langle n' | A^+ | n \rangle = \delta_{n, n'+1} = \delta_{n', n-1}.
\]

Write down ket-bra expansions of \( A \) and \( A^+ \) in this representation, explicitly showing the first few terms of the expansion. Be careful with summation limits. Is \( A \) Hermitian?

Forming ket-bra expansions, we find that
\[
A = \sum_{n, n'=0}^{\infty} |n\rangle \langle n | A | n' \rangle \langle n' | = \sum_{n, n'=0}^{\infty} |n\rangle \delta_{n', n+1} \langle n' | = \sum_{n=0}^{\infty} |n\rangle \langle n + 1 |
\]

the adjoint of which is
\[
A^+ = \sum_{n=0}^{\infty} |n + 1\rangle \langle n |
\]
\[
= |1\rangle \langle 0 | + |2\rangle \langle 1 | + \ldots
\]

which clearly is different from \( A \), so \( A \) is not Hermitian.

(b) Evaluate the action of \( A^+ A \) and \( AA^+ \) on \( |n\rangle \). Explicitly consider the case in which \( n = 0 \).

For \( n > 0 \) we have
\[
A |n\rangle = \sum_{n'=0}^{\infty} |n'\rangle \langle n' | (n' + 1 | n \rangle = \sum_{n'=0}^{\infty} |n'\rangle \delta_{n, n'+1}
\]
\[
= |n - 1\rangle \quad n > 0
\]

Clearly this cannot work for \( n = 0 \), since there isn’t any state. Indeed, for \( n = 0 \), we have
\[
A|0\rangle = (|0\rangle \langle 1 | + |1\rangle \langle 2 | + \ldots) |0\rangle = 0
\]

so the state \( |0\rangle \) is taken onto the null vector by the operator \( A \). It is also an eigenstate of \( A \) with eigenvalue 0. Similarly, we have
\[
A^+ |n\rangle = \sum_{n'=0}^{\infty} |n+1\rangle \langle n' | n \rangle = \sum_{n'=0}^{\infty} |n+1\rangle \delta_{n, n'}
\]
\[
= |n+1\rangle
\]

for all \( n = 0, 1, 2, \ldots \). Thus, we find that \( AA^+ |n\rangle = A |n+1\rangle = |n\rangle \) for all \( n \). That is
\[
AA^+ = 1.
\]

On the other hand \( A^+ A |n\rangle = A^+ |n - 1\rangle \) only for \( n > 0 \). For these states \( A^+ A |n\rangle = A^+ |n - 1\rangle = |n\rangle \), does give the original state back, but \( A^+ A |0\rangle = A^+ 0 = 0 \). You can’t come back from the null vector. It is readily verified that \( A^+ A = 1 - |0\rangle \langle 0 | \). Since they don’t give the state back for all \( n \), \( A \) and \( A^+ \) are not inverses.

(c) Is \( A \) the inverse of \( A^+ \)? Is \( A \) unitary? Is \( A \) normal? (Recall: An operator \( A \) is normal if \( [A, A^+] = 0 \). Be careful.)

We have seen that \( A \) and \( A^+ \) are not inverses of each other. Thus they are not unitary. Also, it is clear that \( AA^+ = 1 \) and \( A^+ A = 1 - |0\rangle \langle 0 | \) are not the same, so \( [A, A^+] \neq 0 \). The operators \( A \) and \( A^+ \) are not normal.
23. In a 2-dimensional space $S$ spanned by the orthonormal vectors $|1\rangle$ and $|2\rangle$, a certain linear operator $A$ has the action $A|2\rangle = -i|1\rangle$ and $A|1\rangle = i|2\rangle$.

(a) Construct the matrix $[A]$ representing the operator $A$ in this representation. Is $A$ Hermitian? Is $A$ Unitary?

Orthonormality implies $\langle 1|1 \rangle = 1 = \langle 2|2 \rangle$ and $\langle 1|2 \rangle = 0 = \langle 2|1 \rangle$. The matrix representing $A$ in this basis has elements $A_{11} = i\langle 1|2 \rangle = 0$, $A_{22} = -i\langle 2|1 \rangle = 0$, $A_{12} = -i\langle 1|1 \rangle = -i$, and $A_{21} = i\langle 2|2 \rangle = i$. Thus

$$[A] = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = [A]^+$$

Thus $A$ is Hermitian. It is easily verified that $[A] = [A]^+[A] = [A][A]^+ = [1]$, so $A$ is also unitary.

(b) Let $B$ be the linear operator that happens to be represented in this basis by a matrix $[B] = [A]^*$ that is the complex conjugate of that representing $A$. Construct $[B]$.

$$[B] = [A]^* = \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -[A]$$

(c) Let $|\phi_1\rangle = i|1\rangle$ and $|\phi_2\rangle = |2\rangle$, be a new set of basis vectors. Show that these two new vectors are orthonormal.

We evaluate

$$\langle \phi_1 | \phi_2 \rangle = -i \langle 1|2 \rangle = 0$$
$$\langle \phi_1 | \phi_1 \rangle = -i \langle 1|1 \rangle = 1$$
$$\langle \phi_1 | \phi_2 \rangle = \langle 2|2 \rangle = 1$$

(d) Construct the matrices $[A']$ and $[B']$ representing the operators $A$ and $B$ in this new basis, and show that $[B'] \neq [A']^*$.

In this new basis

$$[A'] = \begin{bmatrix} \langle \phi_1 | A | \phi_1 \rangle & \langle \phi_2 | A | \phi_2 \rangle \\ \langle \phi_2 | A | \phi_1 \rangle & \langle \phi_2 | A | \phi_2 \rangle \end{bmatrix} = \begin{bmatrix} (i) (-i) \langle 1|A|1 \rangle & (-i) \langle 1|A|2 \rangle \\ (i) \langle 2|A|1 \rangle & \langle 2|A|2 \rangle \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$$

$$[B'] = \begin{bmatrix} \langle \phi_1 | B | \phi_1 \rangle & \langle \phi_2 | B | \phi_2 \rangle \\ \langle \phi_2 | B | \phi_1 \rangle & \langle \phi_2 | B | \phi_2 \rangle \end{bmatrix} = \begin{bmatrix} (i) (-i) \langle 1|B|1 \rangle & (-i) \langle 1|B|2 \rangle \\ (i) \langle 2|B|1 \rangle & \langle 2|B|2 \rangle \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

which shows that $[B'] \neq [A']^*$. Hence the complex conjugate of a linear operator $A$ is not a well-defined object. In this basis it would imply that $A^* = A$ and in the original basis that $A^* = -A$. 

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24. In a basis of states $|1\rangle$ and $|2\rangle$ we have

$$[H] = \begin{pmatrix}
\epsilon_0 + \Delta & V \\
V & \epsilon_0 - \Delta
\end{pmatrix}.$$ 

(a) We rewrite this as

$$[H] = \begin{pmatrix}
\epsilon_0 + \Delta & V \\
V & \epsilon_0 - \Delta
\end{pmatrix} = [H] = \begin{pmatrix}
\epsilon_0 & 0 \\
0 & \epsilon_0
\end{pmatrix} + \begin{pmatrix}
\Delta & V \\
V & \Delta
\end{pmatrix}$$

$$= \epsilon_0 \begin{pmatrix}1 & 0 \\0 & 1 \end{pmatrix} + \Delta \begin{pmatrix}1 & V/\Delta \\V/\Delta & 1 \end{pmatrix} = \epsilon_0 [1] + \Delta [W]$$

with

$$[W] = \begin{pmatrix}1 & V/\Delta \\V/\Delta & 1 \end{pmatrix} = \begin{pmatrix}1 & \tan \theta \\\tan \theta & 1 \end{pmatrix}$$

where we have set $\tan \theta = v/\Delta$. Any operator commutes with the identity operator, and any non-zero state is an eigenstate of it. Thus, any linear combination of the states $|1\rangle$ and $|2\rangle$ is an eigenstate of $\epsilon_0 [1]$, with eigenvalue $\epsilon_0$. Thus, an eigenstate $|\lambda\rangle = a|1\rangle + b|2\rangle$ of $W$ with eigenvalue $\lambda$ will be an eigenstate of $H$ with eigenvalue $\epsilon_0 + \lambda \Delta$.

(b) The characteristic equation is $\det (W - \lambda) = 0 = \lambda^2 - 1 - \tan^2 \theta$. Thus, $\lambda^2 = 1 + \tan^2 \theta = \sec^2 \theta$, gives $\lambda = \pm \sec \theta$. Constructing a right triangle with sides of length $\Delta$ and $V$, and hypotenuse $\sqrt{\Delta^2 + V^2}$ we find that $\lambda = \pm \sqrt{1 + (V/\Delta)^2}$, which gives the energy eigenvalues of $[H]$ as

$$\epsilon_\pm = \epsilon_0 \pm \sqrt{\Delta^2 + V^2}.$$ 

(c) For $\lambda_+ = \sec \theta$, we solve the eigenvalue equation for $W$

$$\begin{pmatrix}1 - \sec \theta & \tan \theta \\\tan \theta & 1 + \sec \theta \end{pmatrix} \begin{pmatrix}a \\b \end{pmatrix} = \begin{pmatrix}0 \\0 \end{pmatrix}.$$ 

The first line gives $a (1 - \sec \theta) + b \tan \theta = 0$, which reduces to $a (\cos \theta - 1) = -b \sin \theta$. The half-angle identities $\cos \theta - 1 = -2 \sin^2 (\theta/2)$ and $\sin \theta = 2 \sin (\theta/2) \cos (\theta/2)$, reduce this to the relation $a \sin (\theta/2) = b \cos (\theta/2)$. The inspired choice $b = \sin (\theta/2)$ then requires that $a = \cos (\theta/2)$, so that

$$|\epsilon_+\rangle = \cos (\theta/2)|1\rangle + \sin (\theta/2)|2\rangle$$

associated with energy $\epsilon_+ = \epsilon_0 + \sqrt{\Delta^2 + V^2}$.

(d) For $\lambda_- = -\sec \theta$, we solve the eigenvalue equation for $W$

$$\begin{pmatrix}1 + \sec \theta & \tan \theta \\\tan \theta & 1 - \sec \theta \end{pmatrix} \begin{pmatrix}a \\b \end{pmatrix} = \begin{pmatrix}0 \\0 \end{pmatrix}.$$ 

Now the second line gives $a \tan \theta = b (1 - \sec \theta)$, which reduces to $a \sin \theta = b (\cos \theta - 1)$. The half-angle identities reduce this to the relation $a \sin (\theta/2) = -b \sin (\theta/2)$. The choice $b = -\cos (\theta/2)$ then requires that $a = \sin (\theta/2)$, so that

$$|\epsilon_-\rangle = \sin (\theta/2)|1\rangle - \cos (\theta/2)|2\rangle$$

associated with energy $\epsilon_- = \epsilon_0 - \sqrt{\Delta^2 + V^2}$.