KJE-3103: Orbital rotations

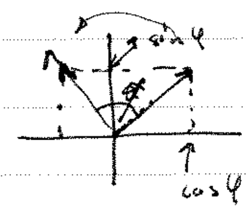
- we frequently need to transform between different sets of orthonormal sets of orbitals, e.g. in optimization and/or response calculations.

- A unitary transformation preserves orthonormality of the orbitals, but does not generally preserve the eigenvectors or eigenvalues of the Hamiltonian!

- An unitary (or othogonal) matrix has the following property: $U^\dagger U = U U^\dagger = 1$, thus (for the real case) the inverse is equal to the transpose.

- A typical unitary/orthogonal matrix is

$$U = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



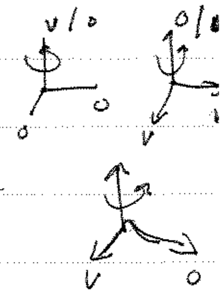
which describes linear rotation of a set of vectors

- Unitary transformations ~~is~~ are thus equivalent to (generalized) rotations

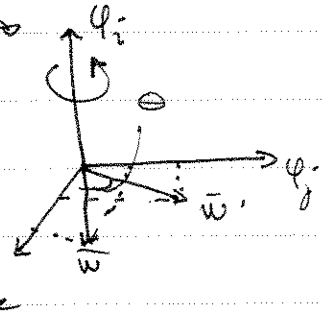
- Consider the wavefunction in Fock-space:

The w.f. is given as a vector in the restricted, N-dimensional, occupied sub-space of the total M-dimensional Fock-space.

- Any rotation ~~which is orthog~~ around an axis orthogonal to the "w.f. vector" preserves ~~both~~ the eigenvalues of the Hamiltonian: i.e.



- thus the rotated w.f. is still described within the same sub-space.



$|\bar{w}| = |\bar{w}'|$

- Thus rotations among occupied orbitals are redundant, in terms of eigenvalues to the Hamiltonian

- Similarly, rotations amongst virtual-virtual orbitals are redundant.

Since the basis vectors are linear combinations of each other, these rotations ensures that the occupied sub-space is ~~span~~ spanned by the same basis vectors before and after the rotations.

- How do we parametrize such rotations in general? We need to generate unitary matices from $M^2/2$ <u>independent</u> parameters.

- The parameters of U cannot be used directly since they are strictly coupled (constrained) by the unitary condition.

- A general, unconstrained unitary matrix can be constructed as

$$U = \exp(X) \quad \text{wher} \quad X^\dagger = -X \quad \text{(anti-Hermitian)}$$

Any unitary matrix can be written this way!

Any unitary marix can be diagonalized:

$U = V \varepsilon V^\dagger$ $\quad$ V unitary, ε diagonal

$$\varepsilon_k = \exp(i\,\delta_k)$$

$$U = V \exp(\underset{\substack{\uparrow \\ \text{diag, real}}}{i\delta}) V^\dagger = \exp(iV\delta V^\dagger)$$

$iV\delta V^\dagger$ is anti-Hermitian since

$$(iV\delta V^\dagger)^\dagger = (-iV^\dagger \delta V) = -\cancel{i(VV^\dagger)V}$$

$$= \cancel{-iV^\dagger(VV^\dagger)}$$

$$= -iV\delta V^\dagger.$$

- We have: $\exp(X)^\dagger = \exp(X^\dagger) = \exp(-X)$
  (easily veryfied)

if $[A,B]=0$ $\quad \exp(A+B) = \exp(A)\exp(B)$

$$\Rightarrow \exp(X)^\dagger \exp(X) = \exp(-X+X) = \exp(\underline{0}) = 1$$

$$\exp(X)^\dagger = \left[1 + X + \frac{X^2}{2!} + \frac{X^3}{3!} + \dots\right]^\dagger$$
$$= \left[1 + X^{\dagger} + \frac{(X^2)^\dagger}{2!} + \frac{(X^3)^\dagger}{3!} + \dots\right]$$
$$= \left[1 - X + \frac{X^2}{2!} - \frac{X^3}{3!} + \dots\right]$$
$$= \exp(-X) \quad \square$$

- X can be written as $X = \frac{X - X^T}{2} + i\,\frac{X + X^T}{2i}$

$$\Rightarrow X = {}^R X + i\left({}^D X + {}^I X\right)$$

it can be shown that $X \to \tilde{X} \Rightarrow [i\,{}^D\tilde{X}, {}^R\tilde{X} + i\,{}^I\tilde{X}] = 0$

$$U = \exp(i\,{}^D\tilde{X})\exp({}^R\tilde{X} + {}^I_i\tilde{X})$$

complex phase shift; often redundant!

Mostly real orthogonal transforms are interesting

$QQ^T = 1 = Q^T Q$ $\quad \Rightarrow R = \exp({}^R X)$

for real orb. rot.

Evaluation of matrix exponentials

- The series $\sum_{n=0}^{\infty} \frac{1}{n!} X^n$, is very rapidly convergent, if $\| X \| < \underline{1}$.

- Alternatively X can be diagonalized:

$$X = i V \delta V^\dagger \qquad V V^\dagger = \underline{1}$$

$$U = \exp(X) = \exp(i V \delta V^\dagger) = V \exp(i\delta) V^\dagger$$

easily evaluated
+ back transform.

Unitary spin-orbital transformations

- we have studied the properties of unitary matrices and linear vector spaes, but how do we transform our spin-orbitals in Fock-space?

- Given a set of orthonormal spin-orbitals φ_q we can find a new set thoug

$$\tilde{\varphi}_q = \sum_p \varphi_p U_{pq}$$

wher the unitary matrix U can be parametrized as

$$U = \exp(-\kappa) \quad \kappa^\dagger = -\kappa$$

- what about Fock-space?

- In Fock-space we need to consider the effect of the tranformation on the annihilation and creation operators as well as on the reference state!

- We can operate in Fock-space by introducing the anti-Hermitian operator

$$\hat{\kappa} = \sum_{pq} \kappa_{pq} a_p^\dagger a_q$$

From the operator relation it immediatly follows that $\hat{\kappa}^\dagger = -\kappa$

- We have the same relations for $\hat{\kappa}$ and $\exp(\hat{\kappa})$ as for the matrix equivalenes, sine only the operator commutation relations matter for the algebra.

- The following relations hold in Fock-space:

$$|\tilde{0}\rangle = \exp(-\hat{\kappa})|0\rangle$$

$$\tilde{a}_p^\dagger = \exp(-\hat{\kappa})\, a_p^\dagger \exp(\hat{\kappa})$$
$$\tilde{a}_p = \exp(-\hat{\kappa})\, a_p \exp(\hat{\kappa})$$

$$\Rightarrow \tilde{a}_p|\tilde{0}\rangle = \exp(-\hat{\kappa})\, a_p \exp(\hat{\kappa})\exp(-\hat{\kappa})|0\rangle$$

$$= \exp(-\hat{\kappa})\, a_p |0\rangle$$

- The equivalence between Fock-space and orbital space is easily seen

$$\Phi = |\varphi_{p1}\varphi_{p2}\ldots\varphi_{pN}| \iff |k\rangle = a^\dagger_{p1}a^\dagger_{p2}\ldots a^\dagger_{pN}|0\rangle$$

$$\tilde{\Phi} = |\tilde{\varphi}_{p1}\ldots\tilde{\varphi}_{pN}| \iff |\tilde{k}\rangle = \tilde{a}^\dagger_{p1}\tilde{a}^\dagger_{p2}\ldots\tilde{a}^\dagger_{pN}|0\rangle$$

where

$$\tilde{\Phi} = \sum_{q_1\ldots q_N} U_{p_1q_1}\ldots U_{p_Nq_N}|\phi_{q_1}\ldots\phi_{q_N}|$$

and $$|\tilde{k}\rangle = \sum_{q_1\ldots q_N} U_{q_1p_1}\ldots U_{q_Np_N}\, a^\dagger_{q_1}\ldots a^\dagger_{q_N}|vac\rangle$$

$$\Rightarrow \tilde{a}^\dagger_{p_1}\ldots\tilde{a}^\dagger_{p_N}|vac\rangle = \sum_{q_1\ldots q_N}(\qquad\qquad)|vac\rangle$$

ther is here a one-to-one mapping between the two representations

and thus $\tilde{a}^\dagger_p = \sum_q a^\dagger_q U_{qp} = \sum_q a^\dagger_q \exp(-\kappa)_{qp}$

and similarly for a_p !

$$\exp(A)^{-1} = \exp(-A)$$

$$\exp(-A)\exp(A) = 1 \quad \Leftarrow \quad [A, A] = 0 \quad !$$

$$B\exp(A)B^{-1} = \exp(BAB^{-1})$$

$$\exp(A+B) = \exp(A)\exp(B) \quad \Leftarrow \quad [A, B] = 0$$

$$\exp(-A)\,B\exp(A) = B + [B, A] + \frac{1}{2!}[[B, A], A] + \dots \quad \text{BCH}$$

- The previous representation can be cast into a more convenient, similarity transformed, form

$$\overline{a}_p^\dagger = \exp(-\hat{\kappa})\, a_p^\dagger \exp(\hat{\kappa}) \qquad (1)$$

To show that $\overline{a}_p^\dagger = \tilde{a}_p^\dagger = \sum_q a_p^\dagger \exp(-\hat{\kappa})_{pq}$

we expand (1) using the BCH expansion:

$$\Rightarrow \overline{a}_p^\dagger = a_p^\dagger + [a_p^\dagger, \hat{\kappa}] + \frac{1}{2!}[[a_p^\dagger, \hat{\kappa}], \hat{\kappa}] + \frac{1}{3!}[[[a_p^\dagger, \hat{\kappa}], \hat{\kappa}], \hat{\kappa}] + \ldots$$

$$[a_p^\dagger, \hat{\kappa}] = -\sum_q a_q^\dagger \kappa_{pq}$$

$$[[a_p^\dagger, \hat{\kappa}], \hat{\kappa}] = \sum_q a_q^\dagger [\kappa^2]_{qp}$$

and for the n-fold commutator

$$[\ldots[[a_p^\dagger, \hat{\kappa}], \hat{\kappa}], \ldots] = (-1)^n \sum_q a_q^\dagger [\kappa^n]_{qp}$$

$$\Rightarrow \overline{a}_p^\dagger = \sum_q a_q^\dagger \left(\delta_{pq} - \kappa_{pq} + \frac{1}{2!}\kappa^2 - \ldots + \frac{(-1)^n}{n!}[\kappa^2]_{qp} + \ldots \right)$$

$$= \sum_q a_q^\dagger \exp(-\kappa)_{qp} \qquad \square$$