5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #1 Supplement

Contents

A. Spectroscopic Notation

The language of spectroscopy is very explicit and elegant, capable of describing a wide range of unanticipated situations concisely and unambiguously. The coherence of this language is diligently preserved by a succession of august committees, whose agreements about notation are codified. These agreements are often published as authorless articles in major journals. The following list of citations include the best of these notation-codifying articles.

1. H. N. Russell, A. G. Shenstone, and L. A. Turner, "Report on Notation for Atomic Spectra,"

Phys. Rev. **33**, 900-906 (1929).

At an informal meeting of spectroscopists at Washington in April, 1928, the writers of this report were requested to draw up a scheme for the clarification of spectroscopic notation. After much discussion and correspondence with spectroscopists both in this country and abroad we are able to present the following recommendations.

The analysis of a spectrum can be of three different types. (1) A multiplet, or in many cases a level, analysis. This includes the determination of the types of terms (S, P, D, etc.), the multiplicities, and the inner quantum numbers of the individual levels when possible. (2) A configuration analysis. The description of the electron configuration with which the spectroscopic terms are to be correlated as given by Hund in this book. (3) A series analysis. The identification of series of terms and finding of their limits. A complete notation must be capable of adequately expressing the results of all three types of analysis whether complete or only partial.

2. W. F. Meggers and C. E. Moore, "Report of Subcommittee f (Notation for the Spectra of Diatomic Molecules)"

J. Opt. Soc. Am. **43**, 422-425 (1953).

This report is restricted to a discussion of notation for atomic spectra arising from energy changes associated with transitions of valence electrons in atoms or ions, including hyperfine structures and isotope shifts, but excluding Röntgen spectra in general. Two sets of symbols are required for atomic spectra, one (I) to aid in the presentation of experimental observations of spectral lines and the other (II) for use in the interpretation of spectral lines as transitions between quantized atomic energy states. Before dealing with these symbols a few words will be devoted to the general rule for symbolizing a specific spectrum.

3. F. A. Jenkins, "Report of Subcommittee f (Notation for the Spectra of Diatomic Molecules)"

J. Opt. Soc. Am. **43**, 425-426 (1953).

The first standardization of the nomenclature for band spectra, which was recommended by R. S. Mulliken [*Phys. Rev.* **36**, 611 (1930)] after consultation with leading workers in the field, was an outstanding success. The almost universal adherence to this notation that is found in the literature on the subject during more than twenty years indicates that changes should be made only where real difficulties have arisen. In Mulliken's report certain symbols were definitely recommended for adoption, and others merely suggested. With the perspective of the intervening period, it is now possible to present a scheme which represents the practice of the majority of the current investigators of diatomic spectra, but which includes a few desirable alterations and the change of some former suggestions to recommendations. Where an alteration of the nomenclature given by Mulliken is here proposed, a brief note of explanation is appended.

4. No author, "Report on Notation for the Spectra of Polyatomic Molecules"

J. Chem. Phys. **23**, 1997-2011 (1955).

A satisfactory standardization of notation for diatomic molecules and their spectra already exists [F. A. Jenkins, *J. Opt. Soc. Am. 43*, 425 (1953)]. The problem of standardization for polyatomic molecules is much more complicated, because of the greater number of degrees of freedom for rotation and vibration, and because of the considerable variety of types of symmetry, or *symmetry groups*, to which polyatomic molecules belong, as contrasted with only two types ($C_{\infty v}$ and $D_{\infty h}$ for diatomic molecules. Fortunately, the system used in Herzberg's well-known book on infrared and Raman spectra [G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945] is already very generally accepted, and forms a suitable basis for the standard notation proposed here. However, when one considers the entire range of polyatomic spectroscopy, from ultraviolet to microwave and magnetic resonance spectra, there are several points of notation which need clarification, revision, supplementation, or simply codification and affirmation in a form to which spectroscopists of all wavelengths can conveniently refer. The principal need for supplementation, as compared with Herzberg's book, arises from the consideration of molecules in nontotally-symmetric electronic states, a matter which is especially essential for electronic spectra.

B. Good Quantum Numbers

What is a <u>good</u> quantum number, as opposed to a <u>useful</u> quantum number, or an <u>almost good</u> quantum number? What are basis functions and what is meant by a <u>complete basis set</u>?

Basis functions are eigenfunctions of the operators whose eigenvalues are used as labels. These eigenvalues are useful quantum numbers. A basis set is said to be <u>complete with respect to some operator</u> $\mathbf{A}$ if for all members of the basis set $\{\phi\}$ $\mathbf{A}\phi_i = \sum_j a_j \phi_j$. Note that completeness is relative: a basis set may be complete with respect to one sort of operator, but not another.

A good quantum number corresponds to an operator which has only diagonal matrix elements in <u>any</u> representation in which the Hamiltonian matrix is also diagonal. A sufficient condition for this is that such an operator must commute with the Hamiltonian.

If $(\mathbf{HA} - \mathbf{AH})\psi_i = 0$, then $\mathbf{A}\psi_i - \mathbf{A}_i\psi_i$.

To prove this, assume $(\mathbf{HA} - \mathbf{AH})\psi_i = 0$ and left multiply by ψ_j^* and integrate.

$$\int \psi_j^*(\mathbf{HA} - \mathbf{AH})\psi_i d\tau = 0$$

$$\int \psi_j^* \mathbf{HA}\psi_i d\tau - \int \psi_j^* \mathbf{AH}\psi_i d\tau = 0$$

$$E_j \int \psi_j^* \mathbf{A}\psi_i d\tau - E_i \int \psi_j^* \mathbf{A}\psi_i d\tau = 0$$

Thus either $E_i = E_j$ or $\int \psi_j^* \mathbf{A}\psi_i = 0$. So for any non-degenerate diagonal representation of $\mathbf{H}$, commutation of $\mathbf{A}$ with $\mathbf{H}$ implies that the matrix for $\mathbf{A}$ is also diagonal. A similar argument shows that for basis functions which are eigenfunctions of an operator which commutes with $\mathbf{H}$, the only off-diagonal matrix elements of $\mathbf{H}$ are those between basis functions belonging to the same eigenvalue of the commuting operator.

An almost good quantum number is the eigenvalue of an operator which does not commute with $\mathbf{H}$. If the Hamiltonian matrix is constructed in a basis specified by an almost good quantum number, the only off-diagonal elements of $\mathbf{H}$ will be between functions satisfying the following condition:

$$\frac{\langle\phi_i|\mathbf{H}|\phi_j\rangle}{|\langle\phi_i|\mathbf{H}|\phi_i\rangle - \langle\phi_j|\mathbf{H}|\phi_j\rangle|} \ll 1.$$

This is the condition for the convergence of perturbation theoretic corrections to the energy.

C.   Perturbation Theory and Secular Equations

There is an aura of mystery surrounding perturbation theory. Perturbation methods are seldom recognized as approximate solutions to a secular equation. The solution of a secular equation is what is actually done when a Hamiltonian matrix is diagonalized and eigenvalues and eigenfunctions are obtained. A one to one correspondence can be made of the order of perturbation corrections to both energies and wave functions with a power series expansion of the results of matrix diagonalization. This will be illustrated below for the simple example of a 2×2 matrix.

It is important to keep in mind the approximate nature of both perturbation theory and matrix diagonalization methods. However, the nature of the approximations made are quite different. The Hamiltonian matrix is constructed using a finite basis set. Exact results usually require an infinite basis set. (Note that the complete basis set for rotation, in the absence of spin and angular momenta, and excluding vibration, has a dimension of 2J + 1.) Matrix diagonalization gives the <u>exact</u> result to <u>infinite</u> order of perturbation theory, but for a finite basis set. Perturbation methods formally treat basis sets of <u>infinite</u> order, but generate large numbers of uninteresting empirical parameters which are difficult to interpret or to calculate. The reason for using perturbation methods is not to generate large numbers of constants, but to give a direct, easy, and algebraic method of writing down all possible functional forms for the dependence of observable energy levels on quantum numbers. In molecular spectroscopy, perturbation methods have been drastically overused. The reason for this was the unavailability of computers for matrix diagonalization until after most of spectroscopic theory was formalized. Matrix methods enable considerable theoretical simplification and a <u>uniform</u> treatment of all spectroscopic data, no matter how pathological.

Consider the 2×2 secular equation:

$$
\begin{array}{cc}
 & \psi_1 \qquad \psi_2 \\
\begin{array}{c} \psi_1 \\ \psi_2 \end{array} &
\begin{vmatrix} d - \epsilon & V \\ V & -d - \epsilon \end{vmatrix} = 0
\end{array}
\tag{1}
$$

This corresponds to the 2 level problem

$$\psi_1 \quad \underline{\qquad} \quad E = d \qquad \text{with an interaction (or repulsion) of V between}$$
$$\text{these levels.}$$
$$\psi_2 \quad \underline{\qquad} \quad E = -d$$

The matrix elements are:

$$
\begin{aligned}
\langle \psi_1 | \mathbf{H} | \psi_1 \rangle &= d \\
\langle \psi_2 | \mathbf{H} | \psi_2 \rangle &= -d \\
\langle \psi_1 | \mathbf{H} | \psi_2 \rangle &= \langle \psi_2 | \mathbf{H} | \psi_1 \rangle = V
\end{aligned}
\tag{2}
$$

The eigenvalues of this Hamiltonian matrix are (using the formula for roots of a quadratic equation):

$$
\epsilon^+ = d \left[1 + \left(\frac{V}{d} \right)^2 \right]^{1/2}
$$

$$
\epsilon^- = -d \left[1 + \left(\frac{V}{d} \right)^2 \right]^{1/2}
\tag{3}
$$

If $V \ll d$, then the radical can be expanded in a convergent power series, the first two terms of which are identical to the zero-order energy and the second order energy from perturbation theory.

$$
\epsilon^\pm = \pm d \left[1 + \frac{1}{2} \left(\frac{V}{d} \right)^2 - \frac{1}{8} \left(\frac{V}{d} \right)^4 \cdots \right]
\tag{4}
$$

Compare with $\epsilon^\pm = \pm d \pm \frac{V^2}{2d}$ from perturbation theory. The matrix $\mathbf{T}$, which defines the transformation $\mathbf{T}^\dagger \mathbf{H} \mathbf{T}$ which diagonalized $\mathbf{H}$, is also a 2×2 matrix, the columns of which define the eigenvectors in terms of the basis functions:

$$
\mathbf{T} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \psi^+ \\ \psi^- \end{pmatrix}
$$

$$
\mathbf{T} = \frac{1}{2} \begin{vmatrix} \left[1 + \frac{d}{(d^2 + V^2)^{1/2}} \right]^{1/2} & \left[1 - \frac{d^2}{(d^2 + V^2)^{1/2}} \right]^{1/2} \\ -\left[1 - \frac{d}{(d^2 + V^2)^{1/2}} \right]^{1/2} & \left[1 + \frac{d^2}{(d^2 + V^2)^{1/2}} \right]^{1/2} \end{vmatrix}
\tag{5}
$$

Expansion of these expressions is quite complicated, but could be done carefully collecting terms of identical order in $\left(\frac{V}{d} \right)$.

There is an alternate and elegant approach involving the general form for any orthogonal transformation T which diagonalizes a real symmetric matrix. Consider the transformation as some sort of a rotation through an angle θ.

$$
\mathbf{T} \equiv \begin{pmatrix} \cos \theta & -\sin \theta \\ +\sin \theta & \cos \theta \end{pmatrix}
\tag{6}
$$

Note that $\mathbf{T}^{\dagger}\,\mathbf{T}= \left(\begin{smallmatrix} 1 & 0 \\ 0 & 1 \end{smallmatrix}\right)$, thus $\mathbf{T}^{\dagger} = \mathbf{T}^{-1}$.

We solve for the θ which results in diagonalization of $\mathbf{H}$ by $\mathbf{T}^{\dagger}\mathbf{HT}$. Abbreviating,

$$\mathbf{T} = \begin{pmatrix} c & -s \\ s & c \end{pmatrix}$$

$$\begin{aligned}
\mathbf{T}^{\dagger}\mathbf{HT} &= \begin{pmatrix} c & s \\ -s & c \end{pmatrix} \begin{pmatrix} d & V \\ V & -d \end{pmatrix} \begin{pmatrix} c & -s \\ s & c \end{pmatrix} \\
&= \begin{pmatrix} cd + sV & cV - sd \\ -sd + cV & -sV - cd \end{pmatrix} \begin{pmatrix} c & -s \\ s & c \end{pmatrix} \\
&= \begin{pmatrix} (c^2 - s^2)d + 2csV & (c^2 - s^2)V - 2scd \\ (c^2 - s^2)V - 2csd & -(c^2 - s^2)d - 2scV \end{pmatrix}
\end{aligned} \tag{7}$$

We want the off-diagonal elements to be zero; this determines θ.

$$0 = (c^2 - s^2)V - 2scd \tag{8}$$

so $\frac{2sc}{c^2 - s^2} = \frac{V}{d}$.

Using trigonometric identities,

$$\frac{2cs}{c^2 - s^2} = \frac{\sin 2\theta}{\cos 2\theta} = \tan 2\theta, \text{ so } \tan 2\theta = \frac{V}{d}$$

$$\theta = \frac{1}{2} \tan^{-1}\left\{\frac{V}{d}\right\} \tag{9}$$

$$\tan^{-1} X = X - \frac{X^3}{3} + \frac{X^5}{5} - \dots \tag{10}$$

$$\text{Thus} \quad \theta = \frac{1}{2}\frac{V}{d} - \frac{1}{2}\frac{1}{3}\left(\frac{V}{d}\right)^3 \dots \tag{11}$$

Returning to equation (7) we can now write out the eigenvalues explicitly.

$$\epsilon^{\pm} = \pm(c^2 - s^2)d \pm 2csV \tag{12}$$

but $\cos^2\theta - \sin^2\theta = \cos 2\theta$
and $2\cos\theta\sin\theta = \sin 2\theta$
so

$$\epsilon^{\pm} = \pm d\cos 2\theta \pm V \sin 2\theta \tag{13}$$

and for $|\theta| \ll 1$

$$\sin 2\theta = 2\theta - \frac{(2\theta)^3}{3!} \dots \tag{14a}$$

$$\cos 2\theta = 1 - \frac{(2\theta)^2}{2!} \dots \tag{14b}$$

so

$$\epsilon^{\pm} = \pm d \mp d\frac{\left(2\frac{1}{2}\frac{V}{d}\right)^2}{2!} \pm V\left(2\frac{1}{2}\frac{V}{d}\right)$$

$$= \pm d \mp \frac{1}{2}\frac{V^2}{d} \pm \frac{V^2}{d} = \pm d \pm \frac{V^2}{2d} \tag{15}$$

retaining terms only up to the second power of $\frac{V}{d}$. This agrees exactly with the perturbation theory result. Now to express $\psi^{\pm}$ in terms of ψ_1 and ψ_2.

$$\mathbf{T} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \psi^+ \\ \psi^- \end{pmatrix}$$

so

$$\psi^+ = \cos\theta\,\psi_1 - \sin\theta\,\psi_2$$
$$\psi^- = \sin\theta\,\psi_1 + \cos\theta\,\psi_2 \tag{16}$$
$$\sin\theta = \theta - \frac{\theta^3}{3!}$$
$$\cos\theta = 1 - \frac{\theta^2}{2!}$$

Again we will retain terms only through second order in $\frac{V}{d}$.

So

$$\psi^+ = \left[1 - \frac{1}{2}\left(\frac{V}{2d}\right)^2\right]\psi_1 - \frac{V}{2d}\psi_2$$
$$\psi^- = \frac{V}{2d}\psi_1 + \left[1 - \frac{1}{2}\left(\frac{V}{2d}\right)^2\right]\psi_2$$

Finally,

$$\psi^+ = \left(1 - \frac{1}{2}\left(\frac{V}{2d}\right)^2\right)\psi_1 - \left(\frac{V}{2d}\right)\psi_2$$
$$\psi^- = \left(\frac{V}{2d}\right)\psi_1 + \left(1 - \frac{1}{2}\left(\frac{V}{2d}\right)^2\right)\psi_2 \tag{17}$$

Ordinary perturbation theory through second order gives <u>exactly</u> this result.

D.   Non-Orthonormal Basis Sets

Matrix elements in a non-orthonormal basis are often more convenient to obtain than in an orthonormal basis due to a property of a class of integrals or to an idiosyncrasy of the numerical method chosen for evaluation of integrals.

Write the Schrödinger equation in matrix form for a non-orthogonal and non-normalized basis:

$$\mathbf{H}\psi_i - E\psi_i = 0 \tag{18}$$

left multiplying and integrating

$$\langle\psi_j|\mathbf{H}|\psi_i\rangle - E\langle\psi_j|\psi_i\rangle = 0. \tag{19}$$

Our eigenvalue equation becomes

$$H_{ji} - ES_{ji} = 0 \tag{20}$$

where $\mathbf{S}$ is the "overlap matrix"

$$S_{ij} = \langle\psi_i|\psi_j\rangle. \tag{21}$$

Note that the unknown constant E appears both on and off diagonal, an unpleasant situation because the matrix to be diagonalized contains the unknown eigenvalues. The matrix $\mathbf{S}$ can be put into orthogonal form if a transformation $\mathbf{U}$ can be found such that

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathcal{S}_{ij} \delta_{ij}. \tag{22}$$

Thus we diagonalize $\mathbf{S}$. Note that there are no off-diagonal elements of $\mathcal{S}$: thus $\mathcal{S}$ is the overlap matrix for an orthogonal basis.

$\mathcal{S}$ can be transformed to a normalized basis.

$$\mathcal{S}^{-1/2} \mathcal{S} \mathcal{S}^{-1/2} = \mathbb{1}. \tag{23}$$

Note that this is not an orthogonal transformation, but it is perfectly well specified and "legal".

What do the two transformations do to the Schrödinger equation?

$$\mathcal{S}^{-1/2}\mathbf{U}^\dagger(\mathbf{H} - E\mathbf{S})\mathbf{U}\mathcal{S}^{-1/2} = \mathcal{S}^{-1/2}\mathbf{U}^\dagger \mathbf{H} \mathbf{U}\mathcal{S}^{-1/2} - E\mathbb{1} \tag{24}$$

Thus $\mathcal{S}^{-1/2}\mathbf{U}^\dagger \mathbf{H} \mathbf{U}\mathcal{S}^{-1/2}$ is the Hamiltonian matrix in an orthonormal basis. Its eigenvalues may be found using the diagonalizing transformation $\mathbf{T}$.

Summary:

1. Write $\mathbf{H}$ and $\mathbf{S}$ in non-orthonormal basis.

2. Diagonalize $\mathbf{S}$; this generates the transformation $\mathbf{U}$ and the diagonal $\mathcal{S}$ matrix.

3. Construct $\mathcal{S}^{-1/2}$ which is used for normalization.

4. Construct the transformed Hamiltonian matrix $\mathcal{S}^{-1/2}\mathbf{U}^\dagger \mathbf{H} \mathbf{U}\mathcal{S}^{-1/2}$ and diagonalize to obtain

$$\mathbf{T}^\dagger \mathcal{S}^{-1/2}\mathbf{U}^\dagger \mathbf{H} \mathbf{U}\mathcal{S}^{-1/2}\mathbf{T} = E\mathbb{1}. \tag{25}$$

5. The eigenfunctions $\{\chi_i\}$ (energy basis) may be expressed as a linear combination of the non-orthonormal basis $\{\psi_i\}$

$$\chi = \left(\mathbf{T}^\dagger \mathcal{S}^{+1/2}\mathbf{U}^\dagger\right)\psi. \tag{26}$$

Do you know where the $+1/2$ power of $\mathcal{S}$ comes from?

E. Transformation of Matrix Elements of any Operator into Perturbed Basis Set

One chooses a basis set in order to be able to write the Hamiltonian matrix in a convenient form. Usually the Hamiltonian matrix is then diagonalized in order to obtain the energy eigenvalues and eigenfunctions. Other observables than energy such as the electric dipole moment or the rotational constant are frequently of interest. It is usually convenient to evaluate the matrix elements of operators which correspond to observables other than energy by using the original basis set employed to write the Hamiltonian matrix. Often, the transformation that diagonalizes $\mathbf{H}$ will not diagonalize the matrix representations of other operators. However, we will want to know what are the

expectation values of any operator in the transformed basis in which the Hamiltonian is diagonal. This is necessary because we usually make our observations on energy eigenstates.

Let $\mathbf{A}$ be the matrix that corresponds to any operator; let $\{\phi_i\}$ be the basis set used to construct the matrix elements of $\mathbf{A}$ and $\mathbf{H}$; let $\mathbf{T}$ be the matrix which defines the unitary transformation which diagonalizes $\mathbf{H}$; and let $\{\psi_i\}$ be the eigenfunctions of $\mathbf{H}$. The Schrödinger equation is

$$
\begin{vmatrix} \mathbf{H}_{11} & & \mathbf{H}_{1n} \\ & \ddots & \\ & & \mathbf{H}_{nn} \end{vmatrix} \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_n \end{pmatrix} = E \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \ddots & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{vmatrix} \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_n \end{pmatrix} \tag{27}
$$

Unit Matrix $\underset{\sim}{1}$

$\mathbf{T}\,\mathbf{T}^{\dagger} \equiv \underset{\sim}{1}$ because $\mathbf{T}$ is unitary. We can insert the unit matrix (as $\mathbf{T}\mathbf{T}^{\dagger}$) anywhere in equation (1).

$$
\mathbf{H}\mathbf{T}\mathbf{T}^{\dagger}\underset{\sim}{\phi} = E\mathbf{1}\mathbf{T}\mathbf{T}^{\dagger}\underset{\sim}{\phi} \tag{28}
$$

now left multiply both sides of (2) by $\mathbf{T}^{\dagger}$

$$
(\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T})(\mathbf{T}^{\dagger}\phi) = \mathbf{T}^{\dagger}E\mathbf{1}\mathbf{1}\phi\mathbf{T}^{\dagger}E\phi = E(\mathbf{T}^{\dagger}\phi)
$$

Here we have an eigenvalue equation for the $(\mathbf{T}^{\dagger}\,\mathbf{H}\mathbf{T})$ operator and the $(\mathbf{T}^{\dagger}\,\phi)$ functions. But $(\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T})$ is required to be a diagonal matrix $(\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T})_{ij} = \delta_{ij}E_i$. Thus

$$
\sum_j (\mathbf{T}^{\dagger}\mathbf{H}\mathbf{T})_{ij}(\mathbf{T}^{\dagger}\phi)_j = E(\mathbf{T}^{\dagger}\phi)k
$$

$$
\sum_j \delta_{ij} E_i (\mathbf{T}^{\dagger}\phi)_j = E(\mathbf{T}^{\dagger}\phi)_j
$$

$$
E_j(\mathbf{T}^{\dagger}\phi)_j = E(\mathbf{T}^{\dagger}\phi)_j
$$

so $E_j = E$ and $(\mathbf{T}^{\dagger}\phi)_j = \psi_j$.

We now wish to express the expectation value of an operator $\mathbf{A}$ in terms of the original basis set $\{\phi_i\}$.

The expectation value of $\mathbf{A}$ in the energy representation (i.e., the representation in which the Hamiltonian matrix is diagonal) is by definition

$$
\langle \psi_i | \mathbf{A} | \psi_i \rangle \equiv \overline{A}_i
$$

$$
\text{but} \quad (\mathbf{T}^{\dagger}\phi)_i \equiv \psi_i
$$

$$
(\mathbf{T}^{\dagger}\phi)_i \equiv \sum_k \mathbf{T}^{\dagger}_{ik}\phi_k
$$

$\langle \psi_i | \equiv (\mathbf{T}^{\dagger}\phi)^{\dagger}_i \equiv (\phi^* \,\mathbf{T})_i$ where "$\dagger$" indicates conjugate transpose.

(The definition of a unitary matrix $\mathbf{T}$ is $\mathbf{T}^{\dagger}\mathbf{T} = \underset{\sim}{1}$, thus $\mathbf{T}^{\dagger} = \mathbf{T}^{-1}$.)

$$\overline{A} = \int \sum_j (\phi_j^* T_{ji}) \mathbf{A} \sum_k (\mathbf{T}_{ik}^\dagger \phi_k)$$

$$= \sum_j \sum_k T_{ji} \langle \phi_j | \mathbf{A} | \phi_k \rangle \, \mathbf{T}_{ik}^\dagger$$

$$= \sum_{j,k} T_{ji} A_{jk} \mathbf{T}_{ik}^\dagger \quad \text{Remember } A_{jk} \text{ is written in the } \{\phi_i\} \text{ basis set.}$$

$$= \sum_{jk} \mathbf{T}_{ij}^\dagger A_{jk} T_{ki} \equiv (\mathbf{T}^\dagger \mathbf{A} \mathbf{T})_{ii}$$

We have the prescription for constructing the expectation value of any operator using the convenient basis set we chose to write the Hamiltonian and the transformation needed to diagonalize the Hamiltonian.

Often we will be interested in non-diagonal matrix elements of $\mathbf{A}$ in the $\{\psi\}$ basis. Such matrix elements are often called transition moments:

$$A_{ij} = (\mathbf{T}^\dagger \mathbf{A} \mathbf{T})_{ij}$$