

# Introduction to Electronic Structure Theory

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## 1 Introduction

The purpose of these notes is to give a brief introduction to electronic structure theory and to introduce some of the commonly used notation. Chapters 1-2 of Szabo and Ostlund [1] are highly recommended for this topic.

## 2 What is Electronic Structure Theory?

Electronic Structure Theory describes the motions of electrons in atoms or molecules. Generally this is done in the context of the Born-Oppenheimer Approximation, which says that electrons are so much lighter (and therefore faster) than nuclei that they will find their optimal distribution for any given nuclear configuration. The electronic energy at each nuclear configuration is the potential energy that the nuclei feel, so solving the electronic problem for a range of nuclear configurations gives the potential energy surface.

Because the electrons are so small, one needs to use quantum mechanics to solve for their motion. Quantum mechanics tells us that the electrons will not be localized at particular points in space, but they are best thought of as “matter waves” which can interfere. The probability of finding a single electron at a given point in space is given by  $\Psi^*(x)\Psi(x)$  for its wavefunction  $\Psi$  at the point  $x$ . The wavefunction can be determined by solving the time-independent Schrödinger equation  $\hat{H}\Psi = E\Psi$ . If the problem is time-dependent, then the time-dependent Schrödinger equation  $i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$  must be used instead; otherwise, the solutions to the time-independent problem are also solutions to the time-dependent problem when they are multiplied by the energy dependent phase factor  $e^{-iEt/\hbar}$ . Since we have fixed the nuclei under the Born-Oppenheimer approximation, we solve for the nonrelativistic *electronic* Schrödinger equation:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}, \quad (1)$$

where  $i, j$  refer to electrons and  $A, B$  refer to nuclei. In atomic units, this simplifies to:

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A}{r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B}{R_{AB}} + \sum_{i>j} \frac{1}{r_{ij}}. \quad (2)$$

This Hamiltonian is appropriate as long as relativistic effects are not important for the system in question. Roughly speaking, relativistic effects are not generally considered important for atoms with atomic number below about 25 (Mn). For heavier atoms, the inner electrons are held more tightly to the nucleus and have velocities which increase as the atomic number increases; as these velocities approach the speed of light, relativistic effects become more important. There are various approaches for accounting for relativistic effects, but the most popular is to use relativistic effective core potentials (RECPs), often along with the standard nonrelativistic Hamiltonian above.

### 3 Properties Predicted by Electronic Structure Theory

According to one of the postulates of quantum mechanics (see below), if we know the wavefunction  $\Psi(\mathbf{r}, t)$  for a given system, then we can determine any property of that system, at least in principle. Obviously if we use approximations in determining the wavefunction, then the properties obtained from that wavefunction will also be approximate.

Since we almost always invoke the Born-Oppenheimer approximation, we only have the *electronic* wavefunction, not the full wavefunction for electrons and nuclei. Therefore, some properties involving nuclear motion are not necessarily available in the context of electronic structure theory. To fully understand the details of a chemical reaction, we need to use the electronic structure results to carry out subsequent dynamics computations. Fortunately, however, quite a few properties are within the reach of just the electronic problem. For example, since the electronic energy is the potential energy felt by the nuclei, minimizing the electronic energy with respect to nuclear coordinates gives an equilibrium configuration of the molecule (which may be the global or just a local minimum).

The electronic wavefunction or its various derivatives are sufficient to determine the following properties:

- Geometrical structures (rotational spectra)
- Rovibrational energy levels (infrared and Raman spectra)
- Electronic energy levels (UV and visible spectra)
- Quantum Mechanics + Statistical Mechanics  $\rightarrow$  Thermochemistry ( $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ,  $C_v$ ,  $C_p$ ), primarily gas phase.

- Potential energy surfaces (barrier heights, transition states); with a treatment of dynamics, this leads to reaction rates and mechanisms.
- Ionization potentials (photoelectron and X-ray spectra)
- Electron affinities
- Franck-Condon factors (transition probabilities, vibronic intensities)
- IR and Raman intensities
- Dipole moments
- Polarizabilities
- Electron density maps and population analyses
- Magnetic shielding tensors  $\rightarrow$  NMR spectra

## 4 Postulates of Quantum Mechanics

1. The state of a quantum mechanical system is completely specified by the wavefunction  $\Psi(\mathbf{r}, t)$ .
2. To every observable in classical mechanics, there corresponds a linear, Hermitian operator in quantum mechanics. For example, in coordinate space, the momentum operator  $\hat{P}_x$  corresponding to momentum  $p_x$  in the  $x$  direction for a single particle is  $-i\hbar \frac{\partial}{\partial x}$ .
3. In any measurement of the observable associated with operator  $\hat{A}$ , the only values that will ever be observed are the eigenvalues  $a$  which satisfy  $\hat{A}\Psi = a\Psi$ . Although measurements must always yield an eigenvalue, the state does not originally have to be in an eigenstate of  $\hat{A}$ . An arbitrary state can be expanded in the complete set of eigenvectors of  $\hat{A}$  ( $\hat{A}\psi_i = a_i\psi_i$ ) as  $\Psi = \sum_i c_i\psi_i$ , where the sum can run to infinity in principle. The probability of observing eigenvalue  $a_i$  is given by  $c_i^*c_i$ .
4. The average value of the observable corresponding to operator  $\hat{A}$  is given by

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau}{\int_{-\infty}^{\infty} \Psi^* \Psi d\tau}. \quad (3)$$

5. The wavefunction evolves in time according to the time-dependent Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi}{\partial t} \quad (4)$$

6. The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates. The Pauli exclusion principle is a direct result of this antisymmetry principle.

## 5 Dirac Notation

For the purposes of solving the electronic Schrödinger equation on a computer, it is very convenient to turn everything into linear algebra. We can represent the wavefunctions  $\Psi(\mathbf{r})$  as vectors:

$$|\Psi\rangle = \sum_{i=1}^n a_i |\hat{\Psi}_i\rangle, \quad (5)$$

where  $|\Psi\rangle$  is called a “state vector,”  $a_i$  are the expansion coefficients (which may be complex), and  $|\hat{\Psi}_i\rangle$  are fixed “basis” vectors. A suitable (infinite-dimensional) linear vector space for such decompositions is called a “Hilbert space.”

We can write the set of coefficients  $\{a_i\}$  as a column vector,

$$|\Psi\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}. \quad (6)$$

In Dirac’s “bracket” (or bra-ket) notation, we call  $|\Psi\rangle$  a “ket.” What about the adjoint of this vector? It is a row vector denoted by  $\langle\Psi|$ , which is called a “bra” (to spell “bra-ket”),

$$\langle\Psi| = (a_1^* a_2^* \cdots a_n^*). \quad (7)$$

In linear algebra, the scalar product  $(\Psi_a, \Psi_b)$  between two vectors  $\Psi_a$  and  $\Psi_b$  is just

$$(\Psi_a, \Psi_b) = (a_1^* a_2^* \cdots a_n^*) \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} = \sum_{i=1}^n a_i^* b_i, \quad (8)$$

assuming the two vectors are represented in the same basis set and that the basis vectors are orthonormal (otherwise, overlaps between the basis vectors, i.e., the “metric,” must be included). The quantum mechanical shorthand for the above scalar product in bra-ket notation is just

$$\langle\Psi_a|\Psi_b\rangle = \sum_{i=1}^n a_i^* b_i. \quad (9)$$

Frequently, one only writes the subscripts  $a$  and  $b$  in the Dirac notation, so that the above dot product might be referred to as just  $\langle a|b\rangle$ . The order of the vectors  $\Psi_a$  and  $\Psi_b$  in a dot product matters if the vectors can have complex numbers for their components, since  $(\Psi_a, \Psi_b) = (\Psi_b, \Psi_a)^*$ .

Now suppose that we want our basis set to be *every possible value of coordinate  $x$* . Apart from giving us a continuous (and infinite) basis set, there is no formal difficulty with this. We can then represent an arbitrary state as:

$$|\Psi\rangle = \int_{-\infty}^{\infty} a_x |x\rangle dx. \quad (10)$$

What are the coefficients  $a_x$ ? It turns out that these coefficients are simply the value of the wavefunction at each point  $x$ . That is,

$$|\Psi\rangle = \int_{-\infty}^{\infty} \Psi(x) |x\rangle dx. \quad (11)$$

Since any two  $x$  coordinates are considered orthogonal (and their overlap gives a Dirac delta function), the scalar product of two state functions in coordinate space becomes

$$\langle \Psi_a | \Psi_b \rangle = \int_{-\infty}^{\infty} \Psi_a^*(x) \Psi_b(x) dx. \quad (12)$$

Now we turn our attention to matrix representations of operators. An operator  $\hat{A}$  can be characterized by its effect on the basis vectors. The action of  $\hat{A}$  on a basis vector  $|\hat{\Psi}_j\rangle$  yields some new vector  $|\Psi'_j\rangle$  which can be expanded in terms of the basis vectors so long as we have a complete basis set.

$$\hat{A}|\hat{\Psi}_j\rangle = |\Psi'_j\rangle = \sum_i^n |\hat{\Psi}_i\rangle A_{ij} \quad (13)$$

If we know the effect of  $\hat{A}$  on the basis vectors, then we know the effect of  $\hat{A}$  on any arbitrary vector because of the linearity of  $\hat{A}$ .

$$\begin{aligned} |\Psi_b\rangle = \hat{A}|\Psi_a\rangle &= \hat{A} \sum_j a_j |\hat{\Psi}_j\rangle = \sum_j a_j \hat{A}|\hat{\Psi}_j\rangle = \sum_j \sum_i a_j |\hat{\Psi}_i\rangle A_{ij} \\ &= \sum_i |\hat{\Psi}_i\rangle \left( \sum_j A_{ij} a_j \right) \end{aligned} \quad (14)$$

or

$$b_i = \sum_j A_{ij} a_j \quad (15)$$

This may be written in matrix notation as

$$\begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \quad (16)$$

We can obtain the coefficients  $A_{ij}$  by taking the inner product of both sides of equation 13 with  $\hat{\Psi}_i$ , yielding

$$\begin{aligned} (\hat{\Psi}_i, \hat{A}\hat{\Psi}_j) &= (\hat{\Psi}_i, \sum_k^n \hat{\Psi}_k A_{kj}) \\ &= \sum_k^n A_{kj} (\hat{\Psi}_i, \hat{\Psi}_k) \\ &= A_{ij} \end{aligned} \tag{17}$$

since  $(\hat{\Psi}_i, \hat{\Psi}_k) = \delta_{ik}$  due to the orthonormality of the basis. In bra-ket notation, we may write

$$A_{ij} = \langle i | \hat{A} | j \rangle \tag{18}$$

where  $i$  and  $j$  denote two basis vectors. This use of bra-ket notation is consistent with its earlier use if we realize that  $\hat{A}|j\rangle$  is just another vector  $|j'\rangle$ .

It is easy to show that for a linear operator  $\hat{A}$ , the inner product  $(\Psi_a, \hat{A}\Psi_b)$  for two general vectors (not necessarily basis vectors)  $\Psi_a$  and  $\Psi_b$  is given by

$$(\Psi_a, \hat{A}\Psi_b) = \sum_i \sum_j a_i^* A_{ij} b_j \tag{19}$$

or in matrix notation

$$(\Psi_a, \hat{A}\Psi_b) = (a_1^* a_2^* \cdots a_n^*) \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & A_{22} & \cdots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{n1} & A_{n2} & \cdots & A_{nn} \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ b_n \end{pmatrix} \tag{20}$$

By analogy to equation (12), we may generally write this inner product in the form

$$(\Psi_a, \hat{A}\Psi_b) = \langle a | \hat{A} | b \rangle = \int \Psi_a^*(x) \hat{A}\Psi_b(x) dx \tag{21}$$

Previously, we noted that  $(\Psi_a, \Psi_b) = (\Psi_b, \Psi_a)^*$ , or  $\langle a | b \rangle = \langle b | a \rangle^*$ . Thus we can see also that

$$(\Psi_a, \hat{A}\Psi_b) = (\hat{A}\Psi_b, \Psi_a)^* \tag{22}$$

We now define the *adjoint* of an operator  $\hat{A}$ , denoted by  $\hat{A}^\dagger$ , as that linear operator for which

$$(\Psi_a, \hat{A}\Psi_b) = (\hat{A}^\dagger \Psi_a, \Psi_b) \tag{23}$$

That is, we can make an operator act *backwards* into ‘‘bra’’ space if we take it’s adjoint. With this definition, we can further see that

$$(\Psi_a, \hat{A}\Psi_b) = (\hat{A}\Psi_b, \Psi_a)^* = (\Psi_b, \hat{A}^\dagger \Psi_a)^* = (\hat{A}^\dagger \Psi_a, \Psi_b) \tag{24}$$

or, in bra-ket notation,

$$\langle a|\hat{A}|b\rangle = \langle \hat{A}b|a\rangle^* = \langle b|\hat{A}^\dagger|a\rangle^* = \langle \hat{A}^\dagger a|b\rangle \quad (25)$$

If we pick  $\Psi_a = \hat{\Psi}_i$  and  $\Psi_b = \hat{\Psi}_j$  (i.e., if we pick two basis vectors), then we obtain

$$\begin{aligned} (\hat{A}\hat{\Psi}_i, \hat{\Psi}_j) &= (\hat{\Psi}_i, \hat{A}^\dagger\hat{\Psi}_j) \\ (\hat{\Psi}_j, \hat{A}\hat{\Psi}_i)^* &= (\hat{\Psi}_i, \hat{A}^\dagger\hat{\Psi}_j) \\ A_{ji}^* &= A_{ij}^\dagger \end{aligned} \quad (26)$$

But this is precisely the condition for the elements of a matrix and its adjoint! Thus the adjoint of the matrix representation of  $\hat{A}$  is the same as the matrix representation of  $\hat{A}^\dagger$ .

This correspondence between operators and their matrix representations goes quite far, although of course the specific matrix representation depends on the choice of basis. For instance, we know from linear algebra that if a matrix and its adjoint are the same, then the matrix is called Hermitian. The same is true of the operators; if

$$\hat{A} = \hat{A}^\dagger \quad (27)$$

then  $\hat{A}$  is a Hermitian operator, and all of the special properties of Hermitian operators apply to  $\hat{A}$  or its matrix representation.

## 6 Slater Determinants

An electronic wavefunction for  $N$  particles must be a function of  $4N$  coordinates: for each electron, we have  $x$ ,  $y$ , and  $z$  Cartesian coordinates plus a spin coordinate (sometimes designated  $\omega$ , which can have values  $\alpha$  and  $\beta$ ). The Cartesian coordinates for electron  $i$  are usually denoted by a collective index  $\mathbf{r}_i$ , and the set of Cartesian plus spin coordinates is often denoted  $\mathbf{x}_i$ .

What is an appropriate form for an  $N$ -electron wavefunction? The simplest solution would be a product of one-particle functions (“orbitals”):

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\cdots\chi_N(\mathbf{x}_N). \quad (28)$$

This is referred to as a *Hartree Product*. Since the orbitals  $\chi_i(\mathbf{x}_i)$  depend on spatial *and* spin coordinates, they are called *spin orbitals*. These spin orbitals are simply a spatial orbital times a spin function, i.e.,  $\chi_i(\mathbf{x}_i) = \phi_i(\mathbf{r}_i)|\alpha\rangle$  or  $\chi_i(\mathbf{x}_i) = \phi_i(\mathbf{r}_i)|\beta\rangle$ .

Unfortunately, the Hartree product is not a suitable wavefunction because it ignores the antisymmetry principle (quantum mechanics postulate #6). Since electrons are fermions, the electronic wavefunction must be antisymmetric with respect to the interchange of coordinates of any pair of electrons. This is not the case for the Hartree Product.

If we simplify for a moment to the case of two electrons, we can see how to make the wavefunction antisymmetric:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)]. \quad (29)$$

The factor  $1/\sqrt{2}$  is just to make the wavefunction normalized (we're assuming our individual orbitals are orthonormal). The expression above can be rewritten as a determinant as

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix} \quad (30)$$

Note a nice feature of this; if we try to put two electrons in the same orbital at the same time (i.e., set  $\chi_1 = \chi_2$ ), then  $\Psi(\mathbf{x}_1, \mathbf{x}_2) = 0$ . This is just a more sophisticated statement of the *Pauli exclusion principle*, which is a consequence of the antisymmetry principle!

This strategy can be generalized to  $N$  electrons using determinants.

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}. \quad (31)$$

A determinant of spin orbitals is called a *Slater determinant* after John Slater. By expanding the determinant, we obtain  $N!$  Hartree Products, each with a different sign; the electrons  $N$  electrons are arranged in all  $N!$  possible ways among the  $N$  spin orbitals. This ensures that the electrons are indistinguishable as required by the antisymmetry principle.

Since we can always construct a determinant (within a sign) if we just know the list of the occupied orbitals  $\{\chi_i(\mathbf{x}), \chi_j(\mathbf{x}), \dots, \chi_k(\mathbf{x})\}$ , we can write it in shorthand in a ket symbol as  $|\chi_i\chi_j \cdots \chi_k\rangle$  or even more simply as  $|ij \cdots k\rangle$ . Note that we have dropped the normalization factor. It's still there, but now it's just *implied*!

How do we get the orbitals which make up the Slater determinant? This is the role of Hartree-Fock theory, which shows how to use the Variational Theorem to use those orbitals which minimize the total electronic energy. Typically, the spatial orbitals are expanded as a linear combination of contracted Gaussian-type functions centered on the various atoms (the linear combination of atomic orbitals molecular orbital or LCAO method). This allows one to transform the integro-differential equations of Hartree-Fock theory into linear algebra equations by the so-called Hartree-Fock-Roothan procedure.

How could the wavefunction be made more flexible? There are two ways: (1) use a larger atomic orbital basis set, so that even better molecular orbitals can be obtained; (2) write the



wavefunction as a linear combination of different Slater determinants with different orbitals. The latter approach is used in the post-Hartree-Fock *electron correlation methods* such as configuration interaction, many-body perturbation theory, and the coupled-cluster method.

## 7 Simplified Notation for the Hamiltonian

Now that we know the functional form for the wavefunction in Hartree-Fock theory, let's re-examine the Hamiltonian to make it look as simple as possible. In the process, we will bury some complexity that would have to be taken care of later (in the evaluation of integrals).

We will define a one-electron operator  $h$  as follows

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}, \quad (32)$$

and a two-electron operator  $v(i, j)$  as

$$v(i, j) = \frac{1}{r_{ij}}. \quad (33)$$

Sometimes this is also called  $g(i, j)$ . Note that, in another simplification, we have begun writing  $h(i)$  as shorthand for  $h(\mathbf{x}_i)$ , and  $v(i, j)$  as shorthand for  $v(\mathbf{x}_i, \mathbf{x}_j)$ .

Now we can write the electronic Hamiltonian much more simply, as

$$\hat{H}_{el} = \sum_i h(i) + \sum_{i<j} v(i, j) + V_{NN}. \quad (34)$$

Since  $V_{NN}$  is just a constant for the fixed set of nuclear coordinates  $\{\mathbf{R}\}$ , we will ignore it for now (it doesn't change the eigenfunctions, and only shifts the eigenvalues).

## 8 Matrix Elements of the Hamiltonian and One- and Two-Electron Integrals

Now that we have a much more compact notation for the electronic Hamiltonian, we need to discuss how to evaluate matrix elements of this Hamiltonian in a basis of  $N$ -electron Slater determinants  $\{|I\rangle\}$ . A matrix element between Slater determinants  $|I\rangle$  and  $|J\rangle$  will be written  $\langle I|\hat{H}|J\rangle$ , where we have dropped the “el” subscript on  $\hat{H}$  because we will discuss the electronic Hamiltonian exclusively from this point. Because the Hamiltonian, like most operators in quantum mechanics, is a Hermitian operator,  $\langle I|\hat{H}|J\rangle = \langle J|\hat{H}|I\rangle^*$ .

It would seem that computing these matrix elements would be extremely tedious, because both  $|I\rangle$  and  $|J\rangle$  are Slater determinants which expand into  $N!$  different products of  $N$  orbitals, giving a total of  $(N!)^2$  different terms! However, all but  $N!$  of these terms go to zero because the orbitals are orthonormal. If we were computing a simple overlap like  $\langle I|I\rangle$ , all of the remaining  $N!$  terms are identical and cancel the  $1/N!$  in the denominator from the Slater determinant normalization factor.

If  $|I\rangle$  and  $|J\rangle$  differ, then any term which places electron  $i$  in some orbital  $\chi_p(i)$  in  $|I\rangle$  and a different orbital  $\chi_q(i)$  in  $|J\rangle$  must also go to zero unless the integration over electron  $i$  is not just a simple overlap integral like  $\int \chi_p^*(i)\chi_q(i)d\mathbf{x}_i$ , but involves some operator  $h(i)$  or  $v(i, j)$ . Since a particular operator  $h(i)$  can only affect one coordinate  $i$ , all the other spin orbitals for other electrons  $j$  must be identical, or the integration will go to zero (orbital orthonormality). Hence,  $h(i)$  allows, at most, only one spin orbital to be different in  $|I\rangle$  and  $|J\rangle$  for  $\langle I|h(i)|J\rangle$  to be nonzero. Integration over the other electron coordinates  $i \neq j$  will give factors of one, resulting in a single integral over a single set of electron coordinates  $\mathbf{x}_i$  for electron  $i$ , which is called a *one-electron integral*,

$$\langle p|h(1)|q\rangle = \langle p|h|q\rangle = \int d\mathbf{x}_1 \chi_p^*(\mathbf{x}_1)h(\mathbf{x}_1)\chi_q(\mathbf{x}_1), \quad (35)$$

where  $\chi_p$  and  $\chi_q$  are the two orbitals which is allowed to be different.

Likewise, the operator  $v(i, j)$  allows up to two orbitals to be different in Slater determinants  $|I\rangle$  and  $|J\rangle$  before matrix element  $\langle I|\hat{H}|J\rangle$  goes to zero. Integration over other electron coordinates gives factors of one, leading to an integral over two electronic coordinates only, a *two-electron integral*,

$$\langle pq|v(1, 2)|rs\rangle = \langle pq|rs\rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(\mathbf{x}_1)\chi_q^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_r(\mathbf{x}_1)\chi_s(\mathbf{x}_2). \quad (36)$$

There are other ways to write this integral. The form above, which places the complex conjugate terms on the left, is called “physicist’s notation,” and is usually written in a bra-ket form.

There is a very simple set of rules, called Slater’s rules, which explain how to write matrix elements  $\langle I|\hat{H}|J\rangle$  in terms of these one- and two-electron integrals. Most of quantum chemistry is derived in terms of these quantities.

## References

- [1] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. McGraw-Hill, New York, 1989.