Chapter 1

Introduction and Literature Review

1.1 Naive Electronic Structure Theory

As an entry point into electronic structure theory, let us begin by forgetting what we know about electrons from the standard model of particle physics. From the standpoint of Heisenberg and others developing the new quantum theory in 1925[1] chemical matter was described by nimble, negatively-charged electrons orbiting heavy, positively-charged nuclei. This theory would be conceptually clarified in the following year by Schrödinger's development of wave mechanics,[2–4] which described the possible states of electrons in a molecule as eigenfunctions of the quantum-mechanical Hamiltonian, oscillating in time with a frequency proportional to their energy. In atomic units:

$$\Psi(t) = \Psi e^{-iEt} \qquad \hat{H}\Psi = E\Psi. \tag{1.1}$$

Crudely speaking, this Hamiltonian is derived from its classical counterpart by replacing its momentum variables with del operators divided by the imaginary

unit, $\hat{\mathbf{p}} = \frac{1}{i}\nabla$. It can be written as a sum over one- and two-electron terms

$$\hat{H} = \sum_i^{\text{electrons}} \hat{h}_i + \sum_{i<j}^{\substack{\text{electron} \\ \text{pairs}}} \hat{g}_{ij} \tag{1.2}$$

where the one-electron operator $\hat{h}_i$ describes the kinetic energy of the ith electron and its electrostatic (Coulomb's law) attraction to the nuclei, and the two-electron operator $\hat{g}_{ij}$ describes the Coulombic repulsion between electrons i and j.

$$\hat{h}_i \equiv \tfrac{1}{2}\hat{\mathbf{p}}_i^2 - \sum_A^{\text{nuclei}} \frac{Z_A}{|\mathbf{r}_A - \mathbf{r}_i|} \qquad \hat{g}_{ij} \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1.3}$$

The vector space containing the wavefunction is the system's Hilbert space, $\mathcal{H}$, which in our case is the space of square integrable functions of n position variables, $L^2(\mathbb{R}^{3n})$, one for each electron in the molecule. Since this space is infinite-dimensional, the only way forward in most cases is to determine a basis that approximately spans the states of interest. Here we are helped by the fact that a function of n position variables can be written as a linear combination of products

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \sum_{p_1 \cdots p_n} c_{p_1 \cdots p_n} \, \phi_{p_1}(\mathbf{r}_1) \cdots \phi_{p_n}(\mathbf{r}_n) \tag{1.4}$$

where the one-electron functions or *orbitals* in this expansion span a one-electron Hilbert space, $\mathcal{H}_{\text{e}} = L^2(\mathbb{R}^3)$. More generally, the Hilbert space of a system is always given by a tensor product of the Hilbert spaces for its constituent particles.

$$\mathcal{H} = \mathcal{H}_{\text{e}} \otimes \mathcal{H}_{\text{e}} \otimes \cdots \tag{1.5}$$

In words, this says that the states of a system are spanned by all possible combinations of the states that its components exhibit in isolation. This enables a general strategy for bootstrapping the electronic structure problem:

1. The states of a single electron orbiting a single nucleus are determined by the spherical symmetry of the nuclear potential. These 1s, 2s, 2p, . . . atomic orbitals have analytically known functional forms, and their energy increases with the number of nodal surfaces in the function.

2. Treating the other electrons in a molecule as static fields which partially shield the nuclear charges, the states of individual electrons in a molecule can be described as linear combinations of atomic one-electron functions centered on each nucleus. The dominant contributions to these molecular orbitals come from atomic orbitals with a similar energy, so that the lowest-energy molecular orbital typically looks like a 1s orbital centered on the nucleus of greatest charge, with very little contribution from, say, the 42g orbital of another nuclear center. The higher energy states are linear combinations of higher energy atomic orbitals with increasing numbers of nodes.

3. Finally, the total electronic wavefunction is described by a linear combination of products of these molecular orbitals, and the electronic ground-state will be spanned to a good approximation by products of the low-energy molecular orbitals. When the molecular orbitals are weakly interacting, the mean-field approximation described in step 2 furnishes a good description of their motions, and the ground-state wavefunction will be heavily dominated by the

orbital product of lowest energy. From a statistical perspective, this means that the electron probability density of the wavefunction approximately factors into one-electron densities, because the orbitals are *weakly correlated* for this state.

At the end of this procedure, we have a matrix equation in the product basis.

$$\mathbf{Hc} = E\mathbf{c} \qquad (\mathbf{H})_{PQ} = \langle \phi_{p_1} \cdots \phi_{p_n} | \hat{H} | \phi_{q_1} \cdots \phi_{q_n} \rangle \qquad (1.6)$$

In the limit of a complete expansion, this eigenvalue equation is exactly equivalent to the Schrödinger equation and the coefficients of the solution vector correspond to the components of the wavefunction along our product functions. In order to stack the deck in favor of one product in the expansion, we can determine the molecular orbitals in step 2 to minimize the energy expectation value

$$\langle \phi_1 \cdots \phi_n | \hat{H} | \phi_1 \cdots \phi_n \rangle = \sum_{i=1}^{\text{orbitals}} h_i^i + \sum_{i<j}^{\substack{\text{orbital} \\ \text{pairs}}} g_{ij}^{ij} \qquad (1.7)$$

where we have defined the ubiquitous *one-* and *two-electron integrals*.

$$h_p^q \equiv \langle \phi_p | \hat{h}_1 | \phi_q \rangle = \int d^3\mathbf{r}_1 \, \phi_p^*(\mathbf{r}_1) \hat{h}_1 \phi_q(\mathbf{r}_1) \qquad (1.8)$$

$$g_{pq}^{rs} \equiv \langle \phi_p \phi_q | \hat{g}_{12} | \phi_r \phi_s \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \, \phi_p^*(\mathbf{r}_1) \phi_q^*(\mathbf{r}_2) \hat{g}_{12} \phi_r(\mathbf{r}_1) \phi_s(\mathbf{r}_2) \qquad (1.9)$$

For an orthonormal orbital basis, this minimization leads to an effective Schrödinger equation for one-electron states

$$(\hat{h}_1 + \hat{v}_1)\phi_i(\mathbf{r}_1) = \epsilon_i\,\phi_i(\mathbf{r}_1) \tag{1.10}$$

where $\hat{v}_1$ is the mean electrostatic field of the other electrons in the molecule.

$$\hat{v}_1 \equiv \sum_{j\neq i} \int d^3\mathbf{r}_2\, \frac{\phi_j^*(\mathbf{r}_2)\phi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.11}$$

We complete the bootstrapping cycle by expanding these unknown molecular orbitals in the basis of the atomic orbitals described in step 1 and solving for the expansion coefficients.

The general strategy we have just outlined carries over into modern electronic structure theory, but it is missing two essential ingredients: the spin of the electron, and the antisymmetric permutational symmetry of electrons as fermions.

1.2   Spin

The non-relativistic theory of one-electron states was completed with Pauli's solution of the hydrogen spectrum at the start of 1926.[5] His work concludes with a discussion of the recent work by Goudsmit and Uhlenbeck[6] showing that the anomalous Zeeman splitting of alkali metals could be explained by positing an intrinsic source of angular momentum and magnetism for the electron besides that generated by its orbital motion about the nucleus. This was the electron's spin.

The need for this quantum number had already been understood by Pauli in his analysis of alkali metal spectra at the end of 1924:

> In alkali metals the angular momentum values of the atom, and its energy changes in the presence of an external magnetic field, are appropriately interpreted as the sole working of the optically active electron, and the same situation is thought to be the case in observations of the anomalous Zeeman effect. From this standpoint, the doublet structure of the alkali spectra, as well as the breakdown of Larmor's theorem, must therefore come from some intrinsic, classically non-describable type of two-valuedness that is a characteristic of the optically active electron.[7]

In hindsight, the Stern-Gerlach experiment[8] had already shown in 1922 that the 5s electron of the silver atom was quantized into two magnetic states, whereas the new quantum theory predicted an odd number of states $(0, \pm 1, \pm 2, \ldots)$ for the spatial orbits of a charged particle. This new source of angular momentum was characterized by half-integer values whose eigenfunctions cannot exist in $L^2(\mathbb{R}^3)$.

$$\hat{s}_z \psi = \pm \tfrac{1}{2} \psi \tag{1.12}$$

The new "spinor" part of the electron's state lives in a two-component vector space

$$\hat{s}_z = \begin{pmatrix} \tfrac{1}{2} & 0 \\ 0 & -\tfrac{1}{2} \end{pmatrix} \qquad \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{1.13}$$

where α is the "up" spinor and β is the "down" spinor. The states of individual electrons are therefore described not by orbitals but by *spin-orbitals*:

$$\psi(\mathbf{x}) = \phi(\mathbf{r})\,\omega_\sigma \qquad \omega_\sigma \equiv \begin{cases} \alpha_\sigma & \text{if the spin projection is } +\frac{1}{2} \\ \beta_\sigma & \text{if the spin projection is } -\frac{1}{2} \end{cases} \qquad (1.14)$$

which live in an extended one-electron Hilbert space, $\mathcal{H}_{\mathrm{e}} = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$, whose degrees of freedom are described by a pair of space and spin variables, $\mathbf{x} \equiv (\mathbf{r}, \sigma)$. The spin variable σ refers to the first or second vector component of the spinor, which evaluates to 1 or 0 depending on whether the state is spin-up or spin-down.

Having completed the system of quantum numbers for an electron in a spherical potential with what would eventually be recognized as spin, Pauli was struck with a curious observation:

> By considering the case of strong magnetic fields we can reduce [earlier observations], that the number of electrons in a completed subgroup is the same as the number of corresponding terms in the Zeeman effect of the alkali spectra, to the following more general rule about the occurrence of equivalent electrons in an atom: There can never be two or more equivalent electrons in an atom for which in strong fields the values of all quantum numbers n, l, k, m_l (or, equivalently, n, l, m_l, m_s) are the same. If an electron is present in the atom for which these quantum numbers (in an external field) have definite values, this state is "occupied." ... We cannot give a further justification for this rule, but it seems to be a very plausible one.[9]

This "housing office for equivalent orbits"[10] would remain a mystery until Heisenberg's work on two-electron systems the following year.

1.3 Antisymmetry

In June of 1926, Heisenberg published an article on *The Many-Body Problem and Resonance in Quantum Mechanics*, which sought to address foundational issues arising in his attempts to apply the new quantum theory to the helium atom. In his words, there were three outstanding problems:

> [1.] The aspects of de Broglie's theory of waves that lead to Bose-Einstein statistics appear to have no analogue in quantum mechanics;
> [2.] Ad hoc rules like Pauli's ban on equivalent orbitals cannot be expressed in the current mathematical formalism of quantum mechanics... [3.] Finally there is one known difficulty in the quantitative interpretation of spectra that we should remind ourselves of: The splitting of singlet and triplet states in the spectra of the alkaline earth metals and in helium is too big by an order of magnitude to be explained as a difference in the magnetic interaction energies of two spinning electrons.[11]

By considering two quantum harmonic oscillators and treating them as indistinguishable in the surprising, quasi-metaphysical[12] sense discovered by Bose[13] and Einstein[14] two years prior, Heisenberg found that the eigenstates of the coupled system could exist in symmetric or antisymmetric combinations, and that only the antisymmetric states were consistent with the spectroscopic observations for

helium. This suggested the intriguing possibility that, as a rule, the electronic wavefunction was antisymmetric under particle exchange, and permutationally symmetric electron wavefunctions simply "are not realized in nature."[11] If so, the appropriate basis state would not be the orbital product, which places each electron into its own distinct orbit, but the determinant function:

$$\Phi_{p_1 \cdots p_n}(\mathbf{x}_1, \ldots, \mathbf{x}_n) = \tfrac{1}{\sqrt{n!}} \sum_{\pi} (-)^{\pi} \psi_{p_1}(\mathbf{x}_{\pi_1}) \cdots \psi_{p_n}(\mathbf{x}_{\pi_n}) \qquad (1.15)$$

where $\pi = \pi_1 \cdots \pi_n$ is a permutation of the electron labels $1 \cdots n$ and $(-)^{\pi}$ is its signature. Whenever the same orbital appears twice in this expansion the determinant vanishes, so this provided a mathematical basis for Pauli exclusion. The energy of the antisymmetric product state has the form

$$\langle \Phi_{1 \cdots n} | \hat{H} | \Phi_{1 \cdots n} \rangle = \overset{\text{orbitals}}{\sum_{i=1}} h_i^i + \overset{\substack{\text{orbital} \\ \text{pairs}}}{\sum_{i<j}} \bar{g}_{ij}^{ij} \qquad \bar{g}_{ij}^{ij} \equiv g_{ij}^{ij} - g_{ij}^{ji} \qquad (1.16)$$

which is the same as the product expectation value of Eq. (1.7) except for the new integrals $g_{ij}^{ji} = \langle \psi_i \psi_j | \hat{g}_{12} | \psi_j \psi_i \rangle$. These "exchange interactions" between electrons in orbitals i and j serve to lower the energy by cancelling out part of the Coulomb repulsion where they overlap. The orthogonality of opposite spinors means that this effect only takes place between electrons of the same spin, lowering the energy of high-spin states relative to low-spin ones of the same configuration, as had been observed by Hund.[15] Thus the new theory could also explain the "large force of unknown origin"[10] that was lowering the energy of the triplet states in helium.

1.4 Modern Electronic Structure Theory

Heisenberg's insights laid the foundation for a quantum mechanical treatment of many-electron systems,[11] but the determinant functions needed to describe these antisymmetric states were difficult to work with. This challenge was addressed in a 1932 article by Vladimir Fock, which developed a new mathematical framework for indistinguishable particles that he called *second quantization.*[16] Building on earlier work by Dirac,[17] the new formalism replaced the opaque combinatorial arguments of the previous "first quantized" formalism with transparent algebraic manipulations. Center stage in the new approach was the annihilation operator:

$$(\hat{a}_p \Psi)(\mathbf{x}_2, \ldots, \mathbf{x}_n) \equiv \sqrt{n} \int d^4 \mathbf{x}' \, \psi_p^*(\mathbf{x}') \, \Psi(\mathbf{x}', \mathbf{x}_2, \ldots, \mathbf{x}_n) \qquad (1.17)$$

The meaning this operation becomes clear from its action on a determinant.

$$\hat{a}_{p_k} \Phi_{p_1 \cdots p_k \cdots p_n} = (-)^{k-1} \Phi_{p_1 \cdots p_{k-1} p_{k+1} \cdots p_n} \qquad (1.18)$$

$$\hat{a}_{p_k}^\dagger \Phi_{p_1 \cdots p_{k-1} p_{k+1} \cdots p_n} = (-)^{k-1} \Phi_{p_1 \cdots p_k \cdots p_n} \qquad (1.19)$$

$$\hat{a}_{p_i p_j \cdots}^{q_1 q_2 \cdots} \Phi_{p_1 \cdots p_{i-1} p_i p_{i+1} \cdots p_{j-1} p_j p_{j+1} \cdots p_n} = \Phi_{p_1 \cdots p_{i-1} q_1 p_{i+1} \cdots p_{j-1} q_2 p_{j+1} \cdots p_n}$$

$$(1.20)$$

$$\left(\text{where } \hat{a}_{p_1 \cdots p_h}^{q_1 \cdots q_h} \equiv \hat{a}_{q_1}^\dagger \cdots \hat{a}_{q_h}^\dagger \hat{a}_{p_h} \cdots \hat{a}_{p_1} \right)$$

In words, the annihilation operator deletes a spin-orbital and renormalizes the state. Its adjoint constitutes a *creation operator* which adds a spin-orbital, and we can string these operators together to form an *excitation operator* which substitutes

one set of spin-orbitals in the determinant with another. In each case, an invalid operation, such as creating an occupied state or annihilating an unoccupied state, causes the determinant to vanish. This allows us to expand the wavefunction in terms of single, double, triple, etc. excitations of some "reference determinant"

$$\Psi = \left(c_0 \hat{1} + c_a^i \hat{a}_i^a + (\tfrac{1}{2})^2 c_{ab}^{ij} \hat{a}_{ij}^{ab} + (\tfrac{1}{3!})^2 c_{abc}^{ijk} \hat{a}_{ijk}^{abc} + \cdots \right) \Phi \qquad (1.21)$$

where i, j, k count over states which are occupied in the determinant, a, b, c count over unoccupied states, and we have adopted the Einstein summation convention for summing over repeated indices. For weakly correlated states, the reference determinant can be chosen so that $c_0 \approx 1$ and the coefficients become negligibly small for higher than quadruple excitations, allowing us to truncate this expansion to a good approximation. Second quantization also lends itself to defining new functional forms for the expansion, such as the coupled-cluster exponential.

$$\Psi = \exp(\hat{T})\Phi \qquad \hat{T} \equiv t_a^i \hat{a}_i^a + (\tfrac{1}{2})^2 t_{ab}^{ij} \hat{a}_{ij}^{ab} + (\tfrac{1}{3!})^2 t_{abc}^{ijk} \hat{a}_{ijk}^{abc} + \cdots \qquad (1.22)$$

Finally, by substituting the following decomposition

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \tfrac{1}{\sqrt{n}} \sum_p \psi_p(\mathbf{x}_1) \left(\hat{a}_p \Psi \right)(\mathbf{x}_2, \ldots, \mathbf{x}_n) \qquad (1.23)$$

into a general antisymmetric matrix element of the Hamiltonian, we find that the restriction of $\hat{H}$ to antisymmetric states can be expressed in the following form.

$$\hat{H} = h_p^q \, \hat{a}_q^p + \tfrac{1}{4}\overline{g}_{pq}^{rs} \, \hat{a}_{rs}^{pq} \tag{1.24}$$

It energy expectation value with respect to a generic state is given by

$$\langle\Psi|\hat{H}|\Psi\rangle = h_p^q \gamma_q^p + \tfrac{1}{4}\overline{g}_{pq}^{rs}\gamma_{rs}^{pq} \tag{1.25}$$

in terms of the one- and two-body reduced density matrices.

$$\gamma_{q_1\cdots q_h}^{p_1\cdots p_h} \equiv \langle\Psi|\hat{a}_{q_1\cdots q_h}^{p_1\cdots p_h}|\Psi\rangle \tag{1.26}$$

In principle, all of the information needed to evaluate the energy is contained in the two-body density matrix, but the structure of this tensor is quite important. Truncating the linear expansion of Eq. (1.21) at some excitation level is known to produce artifactual "unlinked" contributions to the density matrix which spoil the qualitative behavior of the energy with respect to system size and independent subsystems. The correct structure with respect to connectivity is defined by the cumulant expansion.[18]

$$\langle\Psi|\hat{Q}|\Psi\rangle = \sum_{k=1}^{n}\sum_{\Pi}^{\mathrm{Part}(\hat{Q},k)}(-)^{\Pi}\langle\Psi|\hat{\Pi}_1|\Psi\rangle_{\mathrm{c}}\cdots\langle\Psi|\hat{\Pi}_k|\Psi\rangle_{\mathrm{c}} \tag{1.27}$$

Here, $\hat{Q}$ is an excitation operator, Π is a partition of the operator string into k parts, $(-)^{\Pi}$ is the signature of the permutation, and the subscript 'c' denotes the connected contributions to the expectation value. The inverse relationship is given by

$$\langle\Psi|\hat{Q}|\Psi\rangle_{\mathrm{c}} = \sum_{k=1}^{n}(-)^{k+1}(k-1)! \sum_{\Pi}^{\mathrm{Part}(\hat{Q},k)} (-)^{\Pi}\langle\Psi|\hat{\Pi}_1|\Psi\rangle\cdots\langle\Psi|\hat{\Pi}_k|\Psi\rangle \qquad (1.28)$$

which defines the electronic density cumulant.

$$\lambda_{q_1\cdots q_n}^{p_1\cdots p_n} \equiv \langle\Psi|\hat{a}_{q_1\cdots q_n}^{p_1\cdots p_n}|\Psi\rangle_{\mathrm{c}} \qquad (1.29)$$

As a concrete example, the three-particle moment cumulant relations are given by the following.

$$\gamma_{stu}^{pqr} = \lambda_{stu}^{pqr} + P_{(st/u)}^{(pq/r)}\lambda_{st}^{pq}\lambda_u^r + P_{(s/t/u)}\lambda_s^p\lambda_t^q\lambda_u^r \qquad (1.30)$$

$$\lambda_{stu}^{pqr} = \gamma_{stu}^{pqr} - P_{(st/u)}^{(pq/r)}\gamma_{st}^{pq}\gamma_u^r + 2P_{(s/t/u)}\gamma_s^p\gamma_t^q\gamma_u^r \qquad (1.31)$$

1.5   Prospectus

Density cumulant theory (DCT) expresses the energy as a functional of the two-body cumulant. The first variant of the theory was proposed by Kutzelnigg in 2006,[19] and was first implemented by Simmonett four years later.[20] The theory was further developed by Sokolov, who developed several new variants.[21–23]

Chapter 2 presents a benchmark study of the ground-state DCT variants, demonstrating that the best variant of the theory to date, ODC-12, consistently

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outperforms the popular CCSD method for the description of thermochemical and kinetic processes. Chapter 3 presents the main contribution of this work, which is the extension of DCT for the description of excited states via linear response theory. We present a theoretical framework for LR-DCT, derive the linear response working equations for the ODC-12 model, as well as the initial implementation and verification of the theory. We also present the linearized variant of our model, which is the first implementation of a linear response theory for the orbital-optimized linearized coupled-cluster doubles (OLCCD) method. The benchmarks of the LR-ODC-12 model compared with EOM-CCSD look very promising. For well-behaved systems, the mean absolute errors are consistently halved by the new method. For the more challenging excited states of ethylene, butadiene, and hexatriene the differences are more stark. In the most extreme case, EOM-CCSD misses the 2^1A_g state of hexatriene by nearly 1 eV, whereas LR-ODC-12 is within 0.15 eV of the reference value and predicts this states energy gap with the 1^1B_u to nearly 0.01 eV. Finally, Chapter 4 presents the algorithms that were used for our study of larger systems, particularly hexatriene.

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