

Physics 221B
Spring 2008
Homework 18
Due Friday, February 15 at 5pm

Reading Assignment: Rest of Notes 27, but you can skip the section on Koopman's theorem; Notes 28; lecture notes for 2/5/08 and 2/7/08.

1. The Hartree-Fock equations can be solved by iteration. A simplification is to average the potentials over angles and spins after they are computed in terms of some approximate orbitals, to make the Schrödinger equation for the next iteration of orbitals into a central force problem. However, as mentioned in class, this averaging is not necessary in the case of completely filled subshells; in this case, rotationally invariant potentials and central force orbitals are self-consistent.

It is a familiar fact that a three-dimensional central force Hamiltonian $H = p^2/2m + V(r)$ has eigenfunctions in the form $R_{n\ell}(r)Y_{\ell m}(\Omega)$, and that the energies only depend on n and ℓ . It turns out that these facts are true for any rotationally invariant Hamiltonian in three dimensions (that is, H need not have the simple kinetic-plus-potential form). This is important in Hartree-Fock theory, because the exchange potential is not an ordinary potential.

(a) In Hartree-Fock theory, the direct potential is given in terms of the orbitals $u_\lambda(\mathbf{r})$ by Eq. (27.90). Suppose that the orbitals are central force orbitals so $\lambda = (n\ell m_\ell m_s)$, and suppose that all subshells are filled. Show that the direct potential is then rotationally invariant, that is, it only depends on $r = |\mathbf{r}|$.

Hint: It is easiest to solve this as a problem in electrostatics. The potential will be rotationally invariant if the charge density is rotationally invariant. To prove the latter fact, use the addition theorem for spherical harmonics, Eq. (13.70). Once the charge density is known the potential can be determined by Gauss's law.

(b) An operator $\hat{K}$ is rotationally invariant if it commutes with all rotation operators,

$$U(\mathbf{R})^\dagger \hat{K} U(\mathbf{R}) = \hat{K}, \quad (1)$$

for all $\mathbf{R} \in SO(3)$. See Eq. (13.3) or (13.13) for the definition of $U(\mathbf{R})$. K is also called a scalar operator (see Sec. 16.3). Let $K(\mathbf{r}, \mathbf{r}')$ be the kernel of the operator $\hat{K}$, so that the

action or $\hat{K}$ on a wave function ψ is

$$(\hat{K}\psi)(\mathbf{r}) = \int d^3\mathbf{r}' K(\mathbf{r}, \mathbf{r}')\psi(\mathbf{r}'). \quad (2)$$

Then the kernel is the $\mathbf{r}$ -space matrix elements of the operator $\hat{K}$,

$$K(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \hat{K} | \mathbf{r}' \rangle. \quad (3)$$

This is precisely the situation we have with the exchange potentials in Hartree-Fock theory, see Eq. (27.92). (If the kernel of the exchange potential is $V_{ex}^{\pm}(\mathbf{r}, \mathbf{r}')$, then we may write the operator as $\hat{V}_{ex}^{\pm}$. See Eq. (27.93) for the definition of the kernel.)

If $\hat{K}$ is rotationally invariant, then we must have

$$\langle \mathbf{r} | U(\mathbf{R})^{\dagger} \hat{K} U(\mathbf{R}) | \mathbf{r}' \rangle = \langle \mathbf{R}\mathbf{r} | \hat{K} | \mathbf{R}\mathbf{r}' \rangle = \langle \mathbf{r} | \hat{K} | \mathbf{r}' \rangle, \quad (4)$$

or,

$$K(\mathbf{r}, \mathbf{r}') = K(\mathbf{R}\mathbf{r}, \mathbf{R}\mathbf{r}'), \quad (5)$$

for all $\mathbf{R} \in SO(3)$. Think of the kernel $K(\mathbf{r}, \mathbf{r}')$ as a function of two vectors in 3D space. According to Eq. (5), if $\hat{K}$ is rotationally invariant, then the value of $K(\mathbf{r}, \mathbf{r}')$ is unchanged if both vectors are rotated by the same rotation. This means that $K(\mathbf{r}, \mathbf{r}')$ is actually only a function of the rotational invariants of the triangle formed by the two vectors $\mathbf{r}$ and $\mathbf{r}'$. The triangle invariants include the lengths of the three sides of the triangle, $r = |\mathbf{r}|$, $r' = |\mathbf{r}'|$, and $|\mathbf{r} - \mathbf{r}'|$, or the three angles of the triangle.

Show that in the case of complete subshells, two exchange potentials $V_{ex}^{\pm}(\mathbf{r}, \mathbf{r}')$ are functions only of the triangle invariants, so that the operators $\hat{V}_{ex}^{\pm}$ are rotationally invariant. Show also that the two exchange potentials (for spin up and spin down orbitals) are equal, so there is only one Hartree-Fock equation (and we can drop the $\pm$).

Parts (a) and (b) of this problem prove that in the case of complete subshells, it is not necessary to average the potentials (direct and exchange), since they automatically turn out to be invariant under rotations and independent of spin.

2. Work out the multiplets (terms) ^{2S+1}L which result from 3 equivalent d electrons. (“Equivalent” means that they all belong to the same subshell.) Check to make sure your answer adds up to the correct number of levels, based on the degeneracy expected in the central field approximation. In the case of vanadium, use Hund’s rules to determine the ground state multiplet. When spin-orbit coupling is turned on, the multiplets split, and the resulting levels are denoted $^{2S+1}L_J$. Which of these represents the ground state of vanadium?

3. Write out the 2P wave functions explicitly for an $(np)^3$ configuration (e.g., nitrogen), that is, as linear combinations of Slater determinants that you may identify by their m -sets (the set of magnetic quantum numbers for electrons in incomplete subshells). You may denote these Slater determinants simply by $|m\text{-set}\rangle$.