**LMU München**
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**Lehrstuhl für Theoretische Nanophysik**
Dr. F. Heidrich-Meisner
F. Dorfner, *Questions: Florian.Dorfner@physik.uni-muenchen.de*

# 7. Exercise Sheet TA1: Theoretical Solid State Physics

To be discussed on Friday, December 6, 2013.

### Exercise 1: Derivation of the Hartree equations from the variational principle

The Hartree equations shall be derived for the case when there is no antisymmetry condition imposed on the wavefunction, i.e. the many-body wavefunction is assumed to be:

$$\psi_N(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2)\cdots\psi_N(\boldsymbol{r}_N). \tag{1}$$

The Hamiltonian for this problem is given by:

$$H = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_i^2 - Ze^2\sum_{\boldsymbol{R}}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{R}|}\right) + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}. \tag{2}$$

a. Show that the expectation value of the Hamiltonian (2) in a state of the form (1) is

$$\begin{aligned}\langle H\rangle = &\sum_i \int d\boldsymbol{r}\psi_i^*(\boldsymbol{r})\left(-\frac{\hbar^2}{2m}\nabla_i^2 + U^{\text{ion}}(\boldsymbol{r})\right)\psi_i(\boldsymbol{r}) \\ &+ \frac{1}{2}\sum_{i\neq j}\int d\boldsymbol{r}d\boldsymbol{r}'\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\left|\psi_i(\boldsymbol{r})\right|^2\left|\psi_j(\boldsymbol{r}')\right|^2,\end{aligned}$$

provided that all the $\psi_i$ satisfy the normalization condition $\int d\boldsymbol{r}\left|\psi_i(\boldsymbol{r})\right|^2 = 1$.

b. Expressing the constraint of normalization for each $\psi_i$ with a Lagrange multiplier $\epsilon_i$, and taking $\delta\psi_i$ and $\delta\psi_i^*$ as independent variations, show that the stationary condition

$$\delta_i\langle H\rangle = 0$$

leads directly to the Hartree equations:

$$-\frac{\hbar^2}{2m}\nabla_i^2\psi_i(\boldsymbol{r}) + U^{\text{ion}}(\boldsymbol{r})\psi_i(\boldsymbol{r}) + \left[e^2\sum_j\int d\boldsymbol{r}'\left|\psi_j(\boldsymbol{r}')\right|^2\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\right]\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r}),$$

where $U^{\text{ion}}(\boldsymbol{r}) = -Ze^2\sum_{\boldsymbol{R}}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{R}|}$.

**Exercise 2: Hartree-Fock theory of the Jellium model**

A simple model for a solid is found when the lattice-periodic potential is replaced by a constantly charged background with charge density $\rho_{\text{pos}} = \frac{Ne}{V}$. The lattice potential is then given by

$$V_G = -\frac{Ne^2}{V}\int \frac{d\boldsymbol{r}}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

and the Hartree-Fock equation for this model is:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_G(\boldsymbol{r}) + \sum_{\boldsymbol{k}'}\int d\boldsymbol{r}'\frac{e^2}{|\boldsymbol{r}-\boldsymbol{r}'|}\left(2\left|\psi_{\boldsymbol{k}'}(\boldsymbol{r}')\right|^2 - \frac{\psi^*_{\boldsymbol{k}'}(\boldsymbol{r}')\psi_{\boldsymbol{k}}(\boldsymbol{r}')\psi_{\boldsymbol{k}'}(\boldsymbol{r})}{\psi_{\boldsymbol{k}}(\boldsymbol{r})}\right)\right]\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \epsilon_{\boldsymbol{k}}\psi_{\boldsymbol{k}}(\boldsymbol{r}).$$

a. Explain the difference to the Hartree-Fock equations given in the lecture.

b. Show that, in the case of plane waves (i.e., $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}}e^{i\boldsymbol{k}\boldsymbol{r}}$), the Hartree (direct) term in the Hartree-Fock equation compensates for the lattice potential $V_G$.

c. Show that plain waves solve the Hartree-Fock equation above.

d. Compute the eigenvalues $\epsilon_{\boldsymbol{k}}$. Use a substitution to take the integral and use the following relation (Fourier transformation of the Coulomb potential):

$$\frac{1}{z} = \frac{1}{V}\sum_k \frac{4\pi}{k^2}e^{i\boldsymbol{k}\boldsymbol{z}}.$$

The remaining sum over $k$-space can be evaluated by transformation to an integral.

**Exercise 3: The Koopmans' theorem**

Consider a system with $N$ electrons. The Hartree-Fock energy is $E_{HF}$.

a. Show that the energy changes according to

$$E_{HF}(N-1) - E_{HF}(N) = -\epsilon_n, \tag{3}$$

upon removing an electron from the $n$-th orbital. Here, $\epsilon_n$ is the eigenvalue from the Hartree-Fock equation.

b. Which assumption has been implicitly made here?

c. Why does Eq. (3) *not* imply $E_{HF} = \sum_n \epsilon_n$?