

Density Functions

Distinguishable Interacting Point particles

Consider N distinguishable interacting point particles and suppose the probability of finding them in the configuration $\{\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N\}$ is given by $P(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)$, where \vec{x}_i is the complete set of coordinates that describe the state of particle i that may include spatial, spin or momentum information or what not. The probability of finding particle 1 in the region \vec{x} around $d\vec{x}$ is then

$$p_1^{(1)}(\vec{x}) = \int P(\vec{x}, \vec{x}_2, \dots, \vec{x}_N) d\vec{x}_2 d\vec{x}_3 \dots d\vec{x}_N \quad (1)$$

We can similarly define *single particle probability density functions* $p_1^{(i)}(\vec{x})$ for each particle i . In general $p_1^{(i)} \neq p_1^{(j)}$ for $i \neq j$, but we do have¹

$$\int p_1^{(i)}(\vec{x}) d\vec{x} = 1 \quad \forall i \quad (2)$$

thus

$$\sum_{i=1}^N \int p_1^{(i)}(\vec{x}) d\vec{x} = N \quad (3)$$

For a pair of particles

$$p_2^{(1,2)}(\vec{x}_1, \vec{x}_2) = \int P(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N \quad (4)$$

Notice $p_2^{(i,j)}$ is only defined for $i \neq j$, thus

$$\sum_{i \neq j} \int p_2^{(i,j)}(\vec{x}_1, \vec{x}_2) d\vec{x}_1 d\vec{x}_2 = N(N-1) \quad (5)$$

So far we have considered the general case of distinguishable interacting particles and haven't been able to get very far. Let's apply these ideas to electrons which are indistinguishable particles.

Indistinguishable Interacting Point particles

For indistinguishable particles, the single particle probability density function (1) is the same for every particle. Equation (2) thus becomes

$$\int N p_1(\vec{x}) d\vec{x} = N \quad (6)$$

In fact, physically it doesn't make sense to talk about the probability density of a specific particle at all, therefore we must define a general *particle probability density function*

$$\rho_1(\vec{x}) = N p_1(\vec{x}) \quad (7)$$

¹Only if \vec{x}_i is a complete set of coordinates for each i

Similarly (5) becomes

$$\int N(N-1)p_2(\vec{x}_1, \vec{x}_2)d\vec{x}_1d\vec{x}_2 = N(N-1) \quad (8)$$

and we define the *pair probability density* function

$$\rho_2(\vec{x}_1, \vec{x}_2) = N(N-1)p_2(\vec{x}_1, \vec{x}_2) \quad (9)$$

The pair density function is VERY non-intuitive. It is difficult to assign a sensible physical meaning to this quantity. First of all, its normalization $N(N-1)$ is the number of non-distinct pairs, which is not physical for indistinguishable particles. Secondly, the pair density doesn't reduce to particle density when the second coordinate is integrated out. Learning to work around this inconvenience is the main focus of the study of indistinguishable particles.

By definition, these density functions have the following properties

1. Normalization

$$\int \rho_1(\vec{x})d\vec{x} = N \quad (10)$$

$$\int \rho_2(\vec{x}_1, \vec{x}_2)d\vec{x}_1d\vec{x}_2 = N(N-1) \quad (11)$$

2. Reduction

$$\int \rho_2(\vec{x}_1, \vec{x}_2)d\vec{x}_2 = (N-1)\rho_1(\vec{x}_1) \quad (12)$$

Electron Density

Definition

We believe that electrons are indistinguishable point particles whose state is completely given by position and spin $\vec{x}_i = \{\vec{r}_i, \sigma_i\}$. Further we think the probability density of an N -electron system is given by the magnitude of some anti-symmetric wave function

$$P(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \quad (13)$$

where

$$\Psi(\vec{x}_2, \vec{x}_1, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \text{ etc.} \quad (14)$$

Therefore we define the *electron density* function as

$$\begin{aligned} \rho(\vec{r}) &= \int \rho_1(\vec{r}, \sigma_1)d\sigma_1 \\ &= N \int \Psi^*(\{\vec{r}, \sigma_1\}, \vec{x}_2, \dots, \vec{x}_N)\Psi(\{\vec{r}, \sigma_1\}, \vec{x}_2, \dots, \vec{x}_N)d\sigma_1d\vec{x}_2 \dots d\vec{x}_N \end{aligned} \quad (15)$$

The spatial part is integrated out because it can't be probed by X-ray diffraction. On the other hand, the *pair density* should include spin, thus we define

$$\begin{aligned} \rho_2(\vec{x}_1, \vec{x}_2) &= N(N-1)p_2(\vec{x}_1, \vec{x}_2) \\ &= N(N-1) \int \Psi^*(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)d\vec{x}_3 \dots d\vec{x}_N \end{aligned} \quad (16)$$

as the *electron pair density* function.

Properties

In addition to the normalization and reduction properties of the density functions, electron density enjoys the added property due to the anti-symmetry of its wave function.

$$\begin{aligned}
P(\vec{x}_1, \vec{x}_1, \vec{x}_3, \dots, \vec{x}_N) &= \lim_{\vec{x}_2 \rightarrow \vec{x}_1} \Psi^*(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \\
&= \lim_{\vec{x}_2 \rightarrow \vec{x}_1} \Psi^*(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi(\vec{x}_2, \vec{x}_1, \vec{x}_3, \dots, \vec{x}_N) \\
&= - \lim_{\vec{x}_2 \rightarrow \vec{x}_1} \Psi^*(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \\
&= -P(\vec{x}_1, \vec{x}_1, \vec{x}_3, \dots, \vec{x}_N) \Rightarrow \\
P(\vec{x}_1, \vec{x}_1, \vec{x}_3, \dots, \vec{x}_N) &= -P(\vec{x}_1, \vec{x}_1, \vec{x}_3, \dots, \vec{x}_N) = 0
\end{aligned} \tag{17}$$

Therefore

$$\rho_2(\vec{x}, \vec{x}) = -\rho_2(\vec{x}, \vec{x}) = 0 \tag{18}$$

That is, the Pauli exclusion principle is a generic property of anti-symmetry of Ψ and the definition $P = \Psi^* \Psi$.

Exchange-Correlation Hole Density

If electrons were non-interacting

$$p_2(\vec{x}_1, \vec{x}_2) = p_1(\vec{x}_1) p_1(\vec{x}_2) \tag{19}$$

thus (16) reduces to

$$\begin{aligned}
\rho_2(\vec{x}_1, \vec{x}_2) &= N p_1(\vec{x}_1) (N-1) p_1(\vec{x}_2) = \frac{N-1}{N} \rho_1(\vec{x}_1) \rho_1(\vec{x}_2) \\
\rho_2(\vec{x}_1, \vec{x}_2) &= \rho_1(\vec{x}_1) \rho_1(\vec{x}_2) \left(1 - \frac{1}{N}\right)
\end{aligned} \tag{20}$$

We hope that when interaction is turned on, ρ_2 is still in the form (20)

$$\rho_2(\vec{x}_1, \vec{x}_2) = \rho_1(\vec{x}_1) \rho_1(\vec{x}_2) (1 + f(\vec{x}_1, \vec{x}_2)) \tag{21}$$

This way we can rewrite

$$\begin{aligned}
\rho_2(\vec{x}_1, \vec{x}_2) &= \rho_1(\vec{x}_1) (\rho_1(\vec{x}_2) + \rho_1(\vec{x}_2) f(\vec{x}_1, \vec{x}_2)) \\
&= \rho_1(\vec{x}_1) (\rho_1(\vec{x}_2) + h_{XC}(\vec{x}_1, \vec{x}_2))
\end{aligned} \tag{22}$$

and interpret as, the interaction between \vec{x}_1 and \vec{x}_2 is proportional to the electron density at \vec{x}_1 times the modulated density of electron at \vec{x}_2 . $\rho_1(\vec{x}_2)$ is modulated due to the presence of electrons at \vec{x}_1 . The modulation term h_{XC} is known as the *exchange-correlation hole density*. Its normalization

$$\begin{aligned}
\int h_{XC}(\vec{x}_1, \vec{x}_2) d\vec{x}_1 d\vec{x}_2 &= \int \frac{\rho_2(\vec{x}_1, \vec{x}_2)}{\rho_1(\vec{x}_1)} - \rho_1(\vec{x}_2) d\vec{x}_1 d\vec{x}_2 \\
&= \frac{(N-1)\rho_1(\vec{x}_1)}{\rho_1(\vec{x}_1)} - N = -1
\end{aligned} \tag{23}$$

The exchange-correlation hole density is our key to understanding the weirdness of $\rho_2(\vec{x}_1, \vec{x}_2)$, we see that its non-intuitive reduction to ρ_1 is what made h_{XC} nice.