Wavefunctions and Probabilities

Single-electron-orbital (or just orbital) spatial probability density:

$$\left|\phi_j\left(x_i,y_i,z_i\right)\right|^2 \equiv \wp_j\left(x_i,y_i,z_i\right)$$

The squared amplitude of the single-electron-orbital is equal to the probability density to find the electron which occupies the j-th orbital at the point x_i, y_i, z_i.

$$\begin{aligned}\phi_j\left(x_i,y_i,z_i\right) &\equiv A_j\left(x_i,y_i,z_i\right)\cdot e^{\imath\cdot\varphi_j\left(x_i,y_i,z_i\right)} \qquad \phi\in\mathbb{C} \qquad A,\varphi,\wp\in\mathbb{R}\\ \wp_j\left(x_i,y_i,z_i\right) &= A_j^2\left(x_i,y_i,z_i\right)\end{aligned}$$

The phase, φ, comes into play in quantum interference effects, such as in bonding- and anti-bonding molecular orbitals.

***N*-electron joint probability density:**

$$\left|\psi\left(x_1,y_1,z_1,x_2,y_2,z_2,\ldots,x_N,y_N,z_N,m_s\left(1\right),m_s\left(2\right),\ldots,m_s\left(N\right)\right)\right|^2 \equiv \wp\left(x_1,y_1,z_1,x_2,y_2,z_2,\ldots,x_N,y_N,z_N,m_s\left(1\right),m_s\left(2\right),\ldots,m_s\left(N\right)\right)$$

The squared amplitude of the N-electron wavefunction is equal to the joint probability density to find one electron at the point x_1, y_1, z_1 with spin $m_s(1)$, another at x_2, y_2, z_2 with spin $m_s(2)$, and so on for N electrons until the last one is at x_N, y_N, z_N with spin $m_s(N)$.

Spatial probability density of the charge:

$$\rho\left(x_i,y_i,z_i\right)\equiv\rho\left(\mathbf{r}_i\right)\equiv\sum_{m_s(1)}\cdots\sum_{m_s(i)}\cdots\sum_{m_s(N)}\int d\mathbf{r}_1\cdots\int\mathbf{r}_{i-1}\int\mathbf{r}_{i+1}\cdots\int\mathbf{r}_N\cdot\wp(\mathbf{r}_1,\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_N,m_s\left(1\right),\ldots,m_s\left(i\right),\ldots,m_s\left(N\right))$$

The probability to density find any electron from a system of N electrons at the point $\mathbf{r}_i \equiv (x_i, y_i, z_i)$ with any spin, $m_s(i)$ is calculated by integrating over all space for the $N-1$ other electrons and summing over all possible spins.

Spatial probability of the charge:

$$dP\left(x_i,y_i,z_i\right)=\rho\left(x_i,y_i,z_i\right)dx_idy_idz_i$$

The differential probability to find any electron of an N-electron system in the volume of the box centered around the point (x_i, y_i, z_i) with sides of length dx_i, dy_i and dz_i is equal to the volume of the box multiplied by the probability density near the center of the box.

Spatial charge density:

$$\rho_e\left(x_i,y_i,z_i\right)=eN\rho\left(x_i,y_i,z_i\right)$$

The density of charge in an N-electron system at the point (x_i, y_i, z_i) is the product of the probability density of the N-electron wavefunction at that point and the total system charge $(e \cdot N)$.