

# Coulomb shift of the photoemission threshold in crystals

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It is pointed out that in most metals the threshold energy for photoemission is lower than the ionization energy of the isolated constituent atoms of the metal. A similar effect has also been observed in semiconductors. An interpretation of this phenomenon is proposed on the basis of the electron-electron Coulomb interaction and delocalization of electrons in a crystal. It is shown on the basis of the model of a metal consisting of monovalent atoms that the shift of the photoemission threshold is determined by the matrix element of the intra-atomic Coulomb interaction of the electrons with different spin orientations. The connection between the effect and the metal–Mott–Hubbard insulator transition is discussed. © 1995 American Institute of Physics.

An interesting feature of electron emission from metals, which has been given virtually no attention in the literature, is that the electronic work function, which in energy units is equal to the long-wavelength photoemission threshold, is always less than the ionization energy of the isolated constituent atoms of the metal.<sup>1,2</sup> This difference in the electron binding energies, which appears when the free atoms are integrated into a crystal, ranges for different elements from 2 to 5 eV, and in each case it is virtually independent of the type of crystal faces, on which the measurements are performed, and the state of the surface itself.

A similar observation for the case of III–V and II–VI “ionic” semiconductors was made by Harrison and Ciraci.<sup>3</sup> They found that the computed values of the photoemission thresholds, obtained on the basis of the LCAO method using the atomic ionization potentials, are approximately 3.8 eV higher than the corresponding experimental values.

It should be noted that the indicated shift of the photoemission threshold is difficult to explain on the basis of standard ideas about the effect of the crystal–vacuum interface. For example, an accurate analysis based on the density functional method shows that in the case of metals the presence of a boundary leads to redistribution of the electron density near the surface and the formation of an electric double layer at the boundary.<sup>4</sup> However, the sign of this dipole potential is such that the potential does not decrease, but rather increases, the electronic work function of the metal. The insensitivity of the effect to the type and state of the surface also suggests that the shift most likely has “volume” and not “surface” origin.

In the present paper we give a simple interpretation of this phenomenon, based on taking into account correctly the electron-electron Coulomb repulsion in crystals. Our assertion can be briefly summarized as follows. As a result of the electron-electron interaction and delocalization of the electrons in the metal or semiconductor, the “intra-

atomic" potential acting on a valence electron in a crystal is substantially different from the potential acting on an electron located in the outer shell of an isolated atom. This difference can be easily understood by considering a crystal consisting of atoms of the same type with one electron in the outer shell (analog of alkali metals).

In the case of an isolated atom the valence electron then "feels" only the potential of the atomic core. The ionization energy of the atom is  $I = -\epsilon_{at}$ , where  $\epsilon_{at}$  is the ground-state energy of the electron in the potential of a singly charged ion. In a crystal the situation is substantially different, despite the fact that the average electron density surrounding each atom is the same in the crystal and in the isolated atom. The point is that the Bloch functions of the valence electrons in the crystal are delocalized and the total density is formed from electronic states with different spin projections. Therefore, a valence electron located near an atom of the crystal "feels" not only the potential of the atomic core, but also the potential of an electron with opposite spin located on the same atom. This repulsive potential is, in our opinion, responsible for the above-mentioned decrease in the work function of the metal.

To analyze this question quantitatively, we introduce the Hamiltonian of the valence electrons in the Wannier representation. We consider only the matrix elements with respect to the Wannier functions centered at the nearest-neighbor lattice sites. The reduced Hamiltonian is

$$\hat{H} = \sum_{i,\sigma} \epsilon_0 \hat{c}_{i,\sigma}^+ \hat{c}_{i,\sigma} + t \sum_{\langle i,j \rangle} (\hat{c}_{i,\sigma}^+ \hat{c}_{j,\sigma} + \text{h.c.}) + U \sum_i \hat{n}_{i,+1/2} \hat{n}_{i,-1/2} + V \sum_{\langle i,j \rangle} \hat{n}_i \hat{n}_j. \quad (1)$$

Here  $\hat{c}_{i,\sigma}^+$  ( $\hat{c}_{i,\sigma}$ ) is the creation (annihilation) operator of an electron with spin projection  $\sigma$  at the  $i$ th atomic center;  $\hat{n}_i = \sum_{\sigma} \hat{n}_{i,\sigma}$  is the operator of the total number of particles at the  $i$ th center;  $\epsilon_0 = t_{ii}$  and

$$t = t_{ij} = \int d^3 \mathbf{r} \varphi^*(\mathbf{r} - \mathbf{R}_i) \hat{H}_0 \varphi(\mathbf{r} - \mathbf{R}_j)$$

are the matrix elements of the crystal potential, and

$$U = \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 |\varphi(\mathbf{r}_1)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\varphi(\mathbf{r}_2)|^2,$$

$$V = \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 |\varphi(\mathbf{r}_1 - \mathbf{R}_i)|^2 \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} |\varphi(\mathbf{r}_2 - \mathbf{R}_j)|^2$$

are the matrix elements of the Coulomb repulsion of the electrons at a single center and at neighboring centers, respectively.

The work function  $\Phi$  is defined as the minimum energy that must be supplied to an electron at  $T=0$  in order to remove it from the metal. If the minimum energy of the electron at infinity is chosen as the zero energy point, then  $\Phi = -\mu$ , where  $\mu$  is the chemical potential of the electrons

$$\mu = E_0(N+1) - E_0(N). \quad (2)$$

Here  $E_0(N)$  is the ground-state energy of  $N$  electrons. For a macroscopic system  $\mu = \partial E_0 / \partial N$  within quantities of order  $O(1/N)$  (for the time being, we ignore the cases in which an insulator or a superconducting gap is present in the electronic spectrum; in those cases  $\mu^+ = E_0(N+1) - E_0(N)$  and  $\mu^- = E_0(N) - E_0(N-1)$  are different).

In our case, in which the number of electrons  $N_e$  is equal to the number of atoms  $N_{\text{at}}$  and to half the total number of accessible single-electron states  $N_{\text{tot}}$ , the valence band will be exactly half-filled. If it is assumed that the crystal lattice is alternating, i.e., it consists of two equivalent sublattices  $A$  and  $B$  such that the nearest neighbors of each atom in the  $A$  lattice are atoms of the  $B$  lattice, then the electronic spectrum will possess an additional symmetry, manifested in the fact that the spectral density of the electrons will be symmetric with respect to the position of the chemical potential of the system. It turns out that in this case the chemical potential can be calculated exactly. With the help of a unitary transformation we go over to the hole representation

$$\hat{c}_{i,\sigma} \rightarrow \hat{a}_{i,\sigma}^+, \quad \hat{c}_{i,\sigma}^+ \rightarrow \hat{a}_{i,\sigma} \quad (3a)$$

for the sites  $i$  belonging to the  $A$  sublattice and

$$\hat{c}_{i,\sigma} \rightarrow -\hat{a}_{i,\sigma}^+, \quad \hat{c}_{i,\sigma}^+ \rightarrow -\hat{a}_{i,\sigma} \quad (3b)$$

for the sites  $i$  belonging to the  $B$  sublattice. The wave function of  $N$  electrons in this case transforms into the wave function of  $N_{\text{tot}} - N$  holes. The transformed Hamiltonian has the form

$$\hat{H}' = (N_{\text{tot}} - 2\hat{N}_h)[\epsilon_0 + U/2 + zV] + \hat{H}\{a_{i,\sigma}^+; \hat{a}_{i,\sigma}\}, \quad (4)$$

where  $\hat{N}_h$  is the operator of the total number of holes,  $z$  is the number of nearest neighbors, and the operator  $\hat{H}\{a_{i,\sigma}^+; \hat{a}_{i,\sigma}\}$  has the same form as the Hamiltonian (1).

Since the transformation is unitary, the eigenvalues of the initial Hamiltonian (1) for  $N$  electrons are identical to the eigenvalues of the Hamiltonian  $\hat{H}'$  for  $N_{\text{tot}} - N$  fermions (holes). Therefore, the ground-state energy of  $N$  electrons is

$$E_0(N) = (2N - N_{\text{tot}})[\epsilon_0 + U/2 + zV] + E_0(N_{\text{tot}} - N). \quad (5)$$

The number of electrons is assumed to be  $N = N_{\text{tot}}/2 + 1 = N_{\text{at}} + 1$ . We then obtain the following expression from Eq. (5):

$$E_0(N_{\text{at}} + 1) - E_0(N_{\text{at}} - 1) = 2[\epsilon_0 + U/2 + zV].$$

Since  $E_0(N_{\text{at}} + 1) - E_0(N_{\text{at}} - 1) = 2\mu$  in the macroscopic limit for the metallic state, we obtain the following expression for the chemical potential:

$$\mu = \epsilon_0 + U/2 + zV. \quad (6)$$

Let us analyze expression (6). First, note that the position of the chemical potential is completely independent of the characteristics of the band spectrum of the valence electrons. This is a direct consequence of the above-noted symmetry of the energy distribution of the electrons relative to the chemical potential of the system when the levels are half-filled. Since the fact of electron-hole symmetry itself does not depend on the values of the parameters characterizing the itinerant motion, the shift  $\mu$  is determined exclusively by the Coulomb contribution, which shifts the center of the spectral density

upward in energy. It is easy to see that this contribution is equal to exactly the frequency-independent Hartree–Fock correction to the self-energy function  $\Sigma(\omega)$  of the electrons. However, the correlation corrections to the self-energy, which have the form of the spectral density but do not change the position of its symmetry center, do not contribute to the chemical potential.

It is obvious that the Hartree–Fock contribution to the energy, which describes the change in the intra-atomic potential as a result of the appearance of an additional repulsion between the valence electrons in the crystal, generally remains unchanged. It should therefore be expected that the indicated tendency for the chemical potential to shift upward in energy is of a general nature and could be responsible for the decrease in the work function even in situations which are substantially different from the model under consideration.

Returning to the analysis of Eq. (6), we note that in taking the “atomic” limit the energy  $\epsilon_0$  approaches the value  $\epsilon_{\text{at}} - zV$ . The negative correction to the energy ( $-zV$ ) is due to the effect of the potential the tails of neighboring ions on an electron located near one of the atomic centers. This correction is compensated for by a corresponding electronic contribution to Eq. (6), which is a consequence of the electrical neutrality of the atoms at a distance greater than the radius of an electron orbit. This compensation, however, is substantial even on scales comparable to the Bohr radius. It can therefore be assumed that in the crystal  $\epsilon_0 + zV \approx \epsilon_{\text{at}}$ . Consequently, the work function of a metal is estimated to be

$$\Phi \approx -(\epsilon_{\text{at}} + U/2). \quad (7)$$

The shift of the photoemission threshold in the metal consisting of monovalent atoms is thus determined mainly by the intra-atomic Coulomb interaction of the electrons with different spin orientations. The factor 1/2 in expression (7) means that the repulsive potential is formed not by the total electron density but only by the density of the electrons with oppositely oriented spin ( $\langle n_{i,-\sigma} \rangle = 1/2$ ).

To give to expression (7) a quantitative meaning, we compare the work function  $\Phi$  with another measured quantity—the ionization energy  $I^{(-1)}$  of a negative ion (electron affinity energy). It is easy to see that on the basis of the model assumptions adopted above  $I^{(-1)} = \epsilon_{\text{at}} - (2\epsilon_{\text{at}} + U) = -(\epsilon_{\text{at}} + U)$ . We therefore have the following relation between  $\Phi$ ,  $I$ , and  $I^{(-1)}$ :  $I^{(-1)} < \Phi < I$ . Expressing  $\Phi$  in Eq. (7) in terms of  $I$  and  $I^{(-1)}$ , we obtain

$$\Phi = (I + I^{(-1)})/2. \quad (8)$$

It is interesting to note that the numerical values obtained for the work functions of alkali metals from Eq. (8) in terms of the well-known experimental values of the potentials  $I$  and  $I^{(-1)}$  are very close to the measured values.

In conclusion, we call attention to the close relation between the effect considered here and the metal–Mott–Hubbard insulator transition.<sup>5,6</sup> Indeed, taking in expression (6) the “atomic” limit ( $\epsilon_0 = \epsilon_{\text{at}}$ ,  $V = 0$ ,  $U \approx \text{const}$ ), we obtain  $\mu = \epsilon_{\text{at}} + U/2$ . This does not mean, however, that the work function for a system of isolated atoms is equal to  $-(\epsilon_{\text{at}} + U/2)$ . The point is that going from a crystal to a system of isolated atoms we inevitably go through the point of the Mott–Hubbard phase transition. After going

through this point, the metal becomes an insulator, and our formalism for calculating the work function is no longer applicable ( $\mu^+$  differs from  $\mu^-$ ). The ionization energy of the insulator in our case of half-filling is equal to  $-\mu^-$ . This quantity can differ substantially from our computed value of  $\mu$ . For example, in the atomic limit  $\mu^- = \epsilon_{\text{at}}$ .

In summary, the substantial differences in the binding energies of electrons in a crystal and in an isolated atom are essentially attributable to the fact that these systems lie on opposite sides of the metal–insulator phase transition point.

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