Relaxation energies in chemisorption spectroscopy

J. W. Gadzuk

National Bureau of Standards, Washington, D.C. 20234

(Received 9 August 1974)

The upward shift in atomic energy levels (or decrease in electron binding energies) which occurs upon sorption of an atom on a metal surface due to polarization of the valence band electrons, is considered. The polarization shift or extra-atomic relaxation energy is treated within the framework established by Hedin, Johansson, and Lundqvist and the results are related to image potential shifts which have been previously discussed in chemisorption theories.

I. INTRODUCTION

Considerable interest has been raised recently concerning the role of polarization or relaxation energy contributions to the apparent core electron binding energies observed in x-ray photoelectron spectroscopy of solids.[1–6] The physical picture of relaxation that has emerged from these studies is the following. If a core electron in a Hartree–Fock orbital with HF energy E_c is removed from the solid, the remaining electrons can readjust to the presence of the positive hole potential, thus lowering their energy. Since the resulting positive charged metal is left in a lower energy state due to the attractive hole potential, the electron which has been removed (say by photoemission with photons of energy $h\nu$) emerges with an energy greater than $h\nu$ above the HF orbital energy. The difference between the observed energy and the HF energy is termed the relaxation energy although polarization energy might be a more appropriate name.[7] If the initial state is defined in terms of the full Hamiltonian of the system (rather than that part obtained within HF), then the initial core state energy is given by

$$E_c'=E_c+\Delta E_r, \tag{1}$$

where ΔE_r is the relaxation energy. In general, ΔE_r is a positive number and E_c is a negative number so the energy level appears higher than in HF or alternatively, the binding energy is smaller. Shirley and Davis[4,5] have partitioned the relaxation effects into domains involving inter-shell, intra-shell, and outer-shell relaxation. Here we will concentrate on outer-shell relaxation of electrons in the metal conduction band, the predominant solid state effect. There are also many intriguing problems related to the dynamics or temporal evolution of the relaxation process.[8–12] These problems are the subjects of forthcoming papers.[13]

In some senses, the valence levels of atoms, either physisorbed or chemisorbed on metal surfaces, can be expected to experience polarization shifts similar in nature to those of the core levels in solids due to the quasilocalized nature of either the atomic virtual states or the surface molecule states of the adsorption complex.[14–20] The concept of relaxation energy shifts in levels of chemisorbed atoms observed in both uv photoemission spectroscopy (UPS)[21,22] and ion neutralization spectroscopy (INS)[23] is becoming well documented. Typically, these shifts are of the order of 1–3 eV.

The purpose of this paper is to relate the work on polarization shifts due to Hedin *et al.*[1–3] to the problem of polarization shifts in chemisorbed atoms. As will be seen, these shifts are none other than the upward image potential shifts discussed quite frequently in previous surface literature.[24–27] The structure of this paper is the following. The basic principles are outlined in Sec. II. The polarization shifts, in terms of image potentials, which result from the general expressions, are given in Sec. III. The effects of orbital size and symmetry are also considered. Discussion of previous experimental work in terms of the polarization shifts obtained here appears in Sec. IV.

II. RELAXATION ENERGY: GENERAL

In order to illustrate the physical principles involved in the polarization shift, it is convenient to consider the classical self-energy of a hole state interacting with its induced screening charge (in a linear response theory). The charge distribution associated with a hole in the HF orbital $\varphi_l(\mathbf{r})$ is $\rho_l(\mathbf{r})=|\varphi_l(\mathbf{r})|^2$. This hole induces a screening or polarization charge[2,3]

$$\rho_{\text{in}}(\mathbf{r})=\int\frac{d^3q}{(2\pi)^3}\exp(-i\mathbf{q}\cdot\mathbf{r})\rho_{\text{in}}(\mathbf{q}) \tag{2a}$$

with

$$\rho_{\text{in}}(\mathbf{q})=[1/\epsilon(q,0)-1]\rho_l(\mathbf{q}), \tag{2b}$$

where $\epsilon(q,0)$ is the static dielectric function of the conduction band and $\rho_l(\mathbf{q})$ is the Fourier transform of the hole charge density. The classical polarization energy due to the interaction of the induced screening charge with the hole is[28]

$$E_{\text{pol}}=\frac{1}{2}\int\rho_{\text{in}}(\mathbf{r})\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho_l(\mathbf{r}')d^3rd^3r', \tag{3}$$

which with Eqs. (2a, b) is easily reduced to

$$E_{\text{pol}}=\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\left[\frac{v(q)}{\epsilon(q,0)}-v(q)\right]\rho_l(\mathbf{q})\rho_l(-\mathbf{q}),\qquad(4)$$

where $v(q)=4\pi e^2/q^2$ and $E_{\text{pol}}=-\Delta E_r$. The individual terms in Eq. (3) have the following meaning. The $v\rho/\epsilon$ term represents the hole potential when an electron in the state φ_l has been removed and the conduction band electrons have completely relaxed in the presence of the hole. On the other hand, the $v\rho$ term represents the hole potential when the band electrons are frozen into their unrelaxed state which occurs when φ_l is occuppied. The difference between these two potentials, averaged over the spatial extent of φ_l is the relaxation energy discussed by Hedin and Lundqvist.[2,3]

Returning to Eqs. (2) and (3), the relaxation energy can also be written as

$$\Delta E_r=-\frac{1}{2}\int d^3r\,\varphi_l^*(\mathbf{r})\left\{\int\frac{d^3q}{(2\pi)^3}d^3r'\right.$$

$$\left.\times\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')]\rho_l(\mathbf{r}')\left[\frac{v(q)}{\epsilon(q,0)}-v(q)\right]\right\}\varphi_l(\mathbf{r}).\qquad(5)$$

Calling

$$\delta V_p(\mathbf{r}-\mathbf{r}')\equiv-\int\frac{d^3q}{(2\pi)^3}\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')]\left[\frac{v(q)}{\epsilon(q,0)}-v(q)\right],$$

the term in braces in Eq. (5) can be identified as

$$V_p(\mathbf{r})\equiv\int d^3r'\rho_l(\mathbf{r}')\delta V_p(\mathbf{r}-\mathbf{r}')\equiv V_p^*-V_{po},\qquad(6)$$

an effective change in the localized level potential due to the polarization of the conduction band when the electron in state φ_l is removed. In Eq. (6), V_p^* is the total potential due to the completely relaxed conduction band in the presence of the hole, whereas V_{po} is the potential due to the unrelaxed band in the presence of the hole, i.e., that potential seen by an electron in the state φ_l when that state is occuppied. Combining Eqs. (5) and (6), an alternate form for the relaxation energy results,

$$\Delta E_r=\frac{1}{2}\int d^3r\,\varphi_l^*(\mathbf{r})V_p(\mathbf{r})\varphi_l(\mathbf{r}),\qquad(7)$$

which is similar in structure and meaning to the expression obtained by Hedin and Johansson.[1]

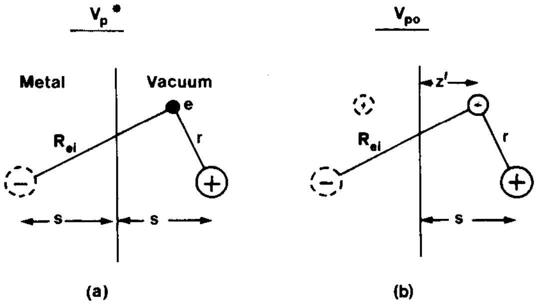

FIG. 1. Schematic model of the effective "core" potential seen by a valence electron of an adsorbed atom. (a) The potential V_p^* which includes relaxation of the surface in the presence of the hole. (b) The potential V_{po} seen by the valence electron when the surface also responds to the occupied level.

III. IMAGE POTENTIALS

The relaxation energy, in either the form given by Eq. (4) or (6), corresponds to the Coulomb self-energy of the test charge interacting with its self-induced screening charge.[29] Within the metal, the screening charge is symmetrically distributed about the hole in a translationally invariant manner. As the position of the hole approaches or passes through the electron gas surface, the screening charge lags behind the hole and ultimately, as the hole potential is far ($\gtrsim$ a few screening lengths) from the surface, the screening charge appears as a surface charge giving rise to the classical image potential energy, $V_{\text{im}}=-e^2/4z'=-3.6/z'$, with V_{im} in eV and z' in Å. In order to make contact with experimentally relevant systems, the normal distance z' from the image plane must be located with respect to either the last plane of ion cores or a model jellium step edge of the smeared-out positive charge background. This location of the origin has been made through detailed considerations of the screening properties at a surface.[30–33] In practice, the image potential must join smoothly onto a potential similar to that one given by Eq. (6) as the test charge moves through the surface.

The image potential can serve as a useful starting approximation for estimating relaxation energies associated with adsorbed atoms on metal surfaces. Referring to Fig. 1, the effective single electron potentials of Eq. (6) are illustrated for two cases in which an adatom is a distance s from the image plane. Figure 1 (a) depicts V_p^*, situation in the fully relaxed state upon removal of a valence electron from the adatom. The potential energy at a point e due to the ion core and the polarization of the solid is $\frac{1}{2}V_p^*=-e^2/r+e^2/R_{ie}$ which is less attractive than when the localized orbital is occuppied because of the electron gas screening of the ion core.[34] For the unrelaxed situation in which the level φ_l is occuppied, Fig. 1(b) applies. In this case, the polarization potential arises from both the repulsive interaction with the ion core image and the attractive interaction with the electrons own image charge. Thus, $\frac{1}{2}V_{po}=-e^2/r+e^2/R_{ie}-e^2/4z'$.[35] Consequently, the polarization potential, Eq. (6), required to calculate the relaxation energy is simply

$$\tfrac{1}{2}V_p(\mathbf{r})\simeq+\frac{e^2}{4z'}=\frac{e^2}{4(z+s)}=\frac{e^2}{4s}\sum_{j=0}^{\infty}(-1)^j\left(\frac{z}{s}\right)^j,\qquad(8)$$

where now the potential is defined in a coordinate system located at the center of the adatom. Combining

Eqs. (6)–(8), the relaxation energy is given by

$$\Delta E_r = \frac{e^2}{4s}\left[1+\sum_{j=1}^{\infty}\frac{(-1)^j}{s^j}e^2\int d^3r\,\varphi_l^*(\mathbf{r})r^j\cos^j\theta\,\varphi_l(\mathbf{r})\right], \quad (9)$$

$$\equiv e^2/4s+\delta E_s(l,m),$$

where the leading term $e^2/4s=3.6/s$ eV is independent of the particular adatom or orbital symmetry and $\delta E_r(l,m)$ is a correction term for adatom orbitals with quantum numbers l, m. For typical adatom–surface separations of 1–2 Å, the leading term in the relaxation energy shifts the observed energy levels upward ~1.5–3.0 eV, in good agreement with previously interpreted spectroscopic data.[22–26] Following the scheme outlined in the appendix, $\delta E_r(s)$ the correction for s orbitals and $\delta E_r(p_i)$ the correction for $p_{i=x,y,z}$ adsorbate orbitals are given by

$$\delta E_r(s) \simeq \frac{e^2}{4s}\sum_{j=1}^{\infty}\frac{1}{(2j+1)}(r_{a/s}),^{2} \quad (10a)$$

$$\delta E_r(p_{x,y}) \simeq \frac{3e^2}{4s}\sum_{j=1}^{\infty}\frac{1}{(2j+3)(2j+1)}(r_{a/s})^{2j}, \quad (10b)$$

$$\delta E_r(p_z) \simeq \frac{3e^2}{4s}\sum_{j=1}^{\infty}\frac{1}{(2j+3)}(r_{a/s})^{2j}, \quad (10c)$$

where the radius of the adatom is approximately r_a and the atom–metal separation $s\gtrsim r_a+n^{-1}$ with n an inverse screening length. Typically, $r_a\lesssim 0.75s$ so the series in Eqs. (10) rapidly converge. The leading terms in Eqs. (10) indicate that $\delta E_r(s)\lesssim 0.2\ e^2/8s$, $\delta E_r(p_{x,y})\lesssim 0.1\ e^2/8s$, and $\delta E_r(p_z)\lesssim 0.25\ e^2/8s$. Implications of these results in terms of experimental findings are discussed in the next section.

IV. DISCUSSION

The results of several different spectroscopic studies[21–27] of adsorbed atoms or molecules on metal surfaces have indicated that image potential or relaxation energy shifts of the order of 1–3 eV are required if the data is to be consistent with chemisorption theory.[14–20] The theory of relaxation shifts presented in this paper indicates that such extra-atomic shifts in core levels or nonbonding valence orbitals are to be expected. Furthermore, the shifts of various sublevels with the same principal quantum number should differ by only $\lesssim 20\%$ with respect to one another.

While the theory of surface relaxation energies presented here has intentionally been simplified, so that contact with notions of image potentials could be made, it is felt that future, more sophisticated treatments will not differ significantly in their physical content,[36] although they may differ quantitatively. Finally, some cautionary words are in order. The image potential matched onto a constant inner potential is an adequate first approximation to the true surface potential, but should not be pushed too far in the quest for theoretical surface relaxation energies. Thus, it does not seem worthwhile to use "better" wave functions for calculating the moments in Eq. (9), since this expression is already limited by the image potential approximation. Neither would it be profitable to "improve" the accuracy of the relative relaxation shifts, Eqs. (10a–c), by including more terms in the sum, since their accuracy is limited by the classical ansatz introduced in the appendix. In spite of these limitations, the theory in its present form is consistent with experimental facts and provides a physical picture of relaxation energies in atoms and molecules chemisorbed on surfaces.

ACKNOWLEDGMENTS

I am grateful to Paul Citrin for straightening me out on some concepts associated with relaxation energies. Useful discussion and hospitality from Stig Lundqvist at the International Centre for Theoretical Physics, Trieste, have also been appreciated.

APPENDIX

The s or p orbital adsorbate wavefunctions considered in Eq. (9) can be written in the form

$$\varphi_l(\mathbf{r})=R_{n,l}(r)p_i(\theta,\varphi)$$

with

$$\begin{aligned} p_s&=1/(4\pi)^{\frac{1}{2}},\\ p_x&=(3/4\pi)^{\frac{1}{2}}\sin\theta\cos\varphi,\\ p_y&=(3/4\pi)^{\frac{1}{2}}\sin\theta\sin\varphi,\\ p_z&=(3/4\pi)^{\frac{1}{2}}\cos\theta. \end{aligned} \quad (\text{A1 a–d})$$

Consequently, the matrix elements are

$$\int d^3r\,\varphi_l^*(\mathbf{r})r^j\cos^j\theta\,\varphi_l(\mathbf{r})$$

$$=\int r^j|R_{n,l}(r)|^2r^2dr\times\int|p_i(\theta,\varphi)|^2\cos^j\theta d\Omega. \quad (\text{A2})$$

Using Eqs. (A1 a–c), it is easy to show that the integrals on Ω in Eq. A2 (defined as I_i) are

$$\begin{aligned} I_s&=1/(j+1),\\ I_z&=3/(j+3),\\ I_{x,y}&=3/[(j+3)(j+1)], \end{aligned}$$

for j an even integer. The integrals vanish for j odd. Since the integrals are nonvanishing only for j even in the sum in Eq. (9),

$$\delta E_r(s)=\frac{e^2}{4s}\sum_{j=1}^{\infty}\frac{1}{(2j+1)}\frac{1}{s^{2j}}\int r^{2j}R^2r^2dr, \quad (\text{A3 a})$$

$$\delta E_r(p_i)=\frac{3e^2}{4s}\sum_{j=1}^{\infty}\frac{1}{(2j+3)}\frac{1}{s^{2j}}\int r^{2j}R^2r^2dr$$

$$\times\left(\frac{1}{(2j+1)}\delta_{i,(x,y)}+\delta_{iz,}\right), \qquad \text{(A3 b)}$$

where the replacement of j by $2j$ takes account of the eveness and the Kronecker delta in Eq. (A3) is unity for $i=$ the orbital orientation in question. In keeping with the spirit of the semiclassical image potential, the radial matrix elements are replaced by $r_a{}^{2j}$, where r_a is the classical atomic radius and Eqs. (10a–c) follow immediately.

---

[1] L. Hedin and G. Johansson, J. Phys. B **2**, 1336 (1969).

[2] L. Hedin and S. Lundqvist Solid State Phys. **23**, 1 (1969).

[3] S. Lundqvist, in *Electrons in Crystalline Solids* (International Atomic Energy Agency Vienna, 1973).

[4] D. A. Shirley, Chem. Phys. Lett. **16**, 220 (1972).

[5] D. W. Davis and D. A. Shirley, J. Elec. Spectrosc. Related Phenomena **3**, 137 (1974).

[6] P. H. Citrin and D. R. Hamann, Chem. Phys. Lett. **22**, 301 (1973).

[7] To me, relaxation implies a dynamic process with some time dependence whereas the polarization or "relaxation" effects discussed here are unrelated to any time scales. Thus, I prefer the term polarization but will stick with convention and use relaxation. I am grateful to Paul Citrin for some useful discussion on this matter.

[8] H. W. Meldner and J. D. Perez, Phys. Rev. A **4**, 1388 (1971).

[9] S. Doniach and M. Šunjić, J. Phys. C **3**, 285 (1970).

[10] E. Müller-Hartman, T. V. Ramakrishnan, and G. Toulouse, Phys. Rev. B **3**, 1102 (1971).

[11] L. Hedin, in Ref. 3.

[12] G. D. Mahan, Solid State Phys. **29**, 75 (1974).

[13] J. W. Gadzuk (to be published).

[14] T. B. Grimley, J. Vac. Sci. Technol. **8**, 31 (1971).

[15] J. R. Schrieffer, J. Vac. Sci. Technol. **9**, 561 (1972).

[16] B. J. Thorpe, Surf. Sci. **33**, 306 (1972).

[17] D. R. Penn, Surf. Sci. **39**, 333 (1973).

[18] M. J. Kelly, J. Phys. C **7**, L157 (1974).

[19] F. Cyrot-Lackmann, M. C. Desjonqueres, and J. P. Gaspard, J. Phys. C. **7**, 925 (1974).

[20] J. W. Gadzuk, Surf. Sci. **43**, 44 (1974); and in *Surface Physics of Crystalline Materials*, edited by J. M. Blakely (Academic, New York, in press).

[21] E. W. Plummer, *34th Annual Conference on Physical Electronics*, (Murray Hill, NJ, 1974).

[22] J. E. Demuth and D. E. Eastman, Phys. Rev. Lett. **32**, 1123 (1974).

[23] H. D. Hagstrum, *2nd International Conference on Solid Surfaces*, Kyoto, Japan, 1974 (to be published in Jap. J. Appl. Phys.).

[24] R. Gomer and L. W. Swanson, J. Chem. Phys. **38**, 1613 (1963).

[25] J. W. Gadzuk, Phys. Rev. B **1**, 2110 (1970).

[26] H. D. Hagstrum and G. E. Becker, Phys. Rev. Lett. **26**, 1104 (1971).

[27] A. C. Hewson and D. M. Newns, Ref. 23.

[28] The factor of $\frac{1}{2}$ arises from the adiabatic switching on of the interaction. See Refs. 1–3 for further discussion.

[29] Using a wavefunction of zero spatial extent $[\rho(q)=1]$ and a Fermi–Thomas dielectric function, Eq. (4) yields $\Delta E_r=\frac{1}{2}e^2\kappa$ with κ the inverse screening length.

[30] J. W. Gadzuk, J. Phys. Chem. Solids **30**, 2307 (1969).

[31] D. M. Newns, J. Chem. Phys. **50**, 4572 (1969).

[32] N. D. Lang, Solid State Phys. **28**, 225 (1973).

[33] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B **6**, 1122 (1972).

[34] For illustrative purposes, the ion core potential has been replaced by a point charge rather than a distribution over the spatial extent of φ_l. This is of no concern here since this term will be cancelled by a similar one in V_{po}.

[35] Note that the image potential energy already includes the factor of $\frac{1}{2}$ in its definition. For a perfect conductor, the "image potential energy" due to an electron at a point $\mathbf{s}=(\theta,0,s)$ is $V_{\text{im}}(s)=(e/2)\int\sigma(\boldsymbol{\varrho})d^2\rho/|\boldsymbol{\varrho}-s|$, where $\sigma(\boldsymbol{\varrho})$ is the real induced surface charge at a point $\boldsymbol{\varrho}$ on the $z=0$ surface. With

$$\sigma=\frac{1}{4\pi}E=\frac{es}{2\pi(\rho^2+s^2)^{\frac{3}{2}}},$$

the familiar form $V_{\text{im}}(s)=e^2/4s$ follows at once. I am grateful to Dave Penn for preventing me from double counting.

[36] A possible exception to this may arise from dynamical image force corrections. For recent work in this area: M. Šunjić, G. Toulouse, and A. Lucas, Solid State Comm. **11**, 1629 (1972); J. Heinrichs, Phys. Rev. B **8**, 1346 (1973); J. Harris and R. O. Jones, J. Phys. C **6**, 3585 (1973).