

Abstract: Can chemisorption bonding shifts be separated from relaxation-energy shifts in photoelectron spectroscopy?

J. W. Gadzuk

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

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Consider the surface-molecule limit of chemisorption in which an adatom orbital with eigenvalue ϵ_a forms a bond with substrate orbitals of energy ϵ_s . The molecular orbital (M) eigenvalues are

$$\epsilon_{\pm} = \{\epsilon_a + \epsilon_s \pm [4V^2 + (\epsilon_a - \epsilon_s)^2]^{1/2}\} / 2, \quad (1)$$

where the hopping integral V causes a chemical bonding shift. In a photoemission experiment from such a MO, the electrons ejected from the bond are observed (upon subtraction of the photon energy) at the energy

$$\epsilon_{\pm}(\text{obs}) = \epsilon_{\pm} + \delta\epsilon_{\pm}(\text{rel}), \quad (2)$$

where $\delta\epsilon_{\pm}(\text{rel})$ is the relaxation energy due to hole creation in the MO state.¹ The problem to be addressed is how to determine a value of V , given $\epsilon(\text{obs})$.

Demuth and Eastman² have analyzed photoemission spectra from CO chemisorbed on Ni under the assumption that the relaxation shift of the nonbonding σ orbitals on CO is identical to the relaxation shift of the bonding π orbitals and (implicitly) that the relaxation shifts of the Ni d orbitals are equal to the nonbonding (clean surface) value. In this approximation scheme, the neglect of the MO charge-cloud distortion due to bonding-charge pileup between the a and s centers is compensated for by allowing each molecular constituent to have its full uncoupled relaxation shift.

To check out the independent atom relaxation energy approximation, the relaxation (or polarization) energy shift for hole creation in a diatomic hydrogen molecule embedded in an electron gas has been calculated³ and the results indicate that the relaxation energy differs by only 2%–9% (depending on electron-gas density in the range $5 \gtrsim r_s \gtrsim 2$) from the uncoupled atom value. Assuming that this difference can be neglected, we can then replace $\epsilon_{\pm}(\text{obs})$ of Eq. (2) by ϵ_{\pm} of Eq. (1) with

$$\epsilon_s \rightarrow \epsilon_s + \delta\epsilon_s(\text{rel}) = \epsilon_s(\text{obs})$$

and

$$\epsilon_a \rightarrow \epsilon_a + \delta\epsilon_a(\text{rel}) = \epsilon_a(\text{obs})$$

where $\delta\epsilon_a(\text{rel})$ is now the extra-atomic or polarization self-energy.^{1,4,5} Within this scheme, the observed MO energy is related to the known quantities $\epsilon_s(\text{obs})$ (from clean surface experiments) and ϵ_a (from gas-phase experiments) and the unknown quantities $\delta\epsilon_a(\text{rel})$ and V by

$$\epsilon_{\pm}(\text{obs}) = \{\epsilon_s(\text{obs}) + \epsilon_a + \delta\epsilon_a(\text{rel}) \pm [4V^2 + \{\epsilon_s(\text{obs}) - \epsilon_a - \delta\epsilon_a(\text{rel})\}^2]^{1/2}\} / 2, \quad (3)$$

Rather than calculate V , we calculate the polarization energy $\delta\epsilon_a(\text{rel})$ for a hole created in an atomic orbital state $\phi_a(\mathbf{r})$ on the adatom located a distance s from the effective image plane of the surface. Following Hedin⁴ and Hodges,⁵ the polarization energy is given by:

$$\delta\epsilon_a(\text{rel}) \approx \int d^3r d^3r' \phi_a^*(\mathbf{r}) \sum(\mathbf{r}, \mathbf{r}'; \epsilon_a) \phi_a(\mathbf{r}') \quad (4a)$$

with the nonlocal self-energy

$$\sum(\mathbf{r}, \mathbf{r}'; \epsilon_a) = \frac{i}{2\pi} \int d\omega G_0(\mathbf{r}, \mathbf{r}'; \epsilon_a - \omega) \frac{\delta V_{\text{ind}}(\mathbf{r}', \omega)}{\delta n(\mathbf{r}, \omega)}, \quad (4b)$$

the ω component of the potential induced at \mathbf{r}' by a charge at

$$\frac{\delta V_{\text{ind}}(\mathbf{r}', \omega)}{\delta n(\mathbf{r}, \omega)} = \frac{e^2}{2\pi} \int d^2q \frac{1 - \epsilon_q(\omega)}{1 + \epsilon_q(\omega)} \frac{\exp[iq \cdot (\mathbf{r}' - \mathbf{r}_{\parallel})] \exp[-q(|z| + |z'|)]}{q}, \quad (4c)$$

with $\epsilon_q(\omega)$ the electron-gas dielectric function, \mathbf{r}_{\parallel} and \mathbf{q} lying in the plane of the surface, and G_0 the hole Green's function.

Taking $\epsilon_q(\omega) \approx 1 - \omega_p^2/\omega^2$ with ω_p the bulk plasmon frequency and neglecting dynamic and van der Waals polarization, the system of Eqs.(4) can be reduced to⁶

$$\delta\epsilon_a(\text{rel}) \approx \frac{e^2}{2} \int dq \left| \int_{-\infty}^{+\infty} dz \exp(-q|z|) \rho(q; z) \right|^2, \quad (5a)$$

where

$$\rho(q, z) = \int d^2r_{\parallel} |\phi_a(\mathbf{r}_{\parallel}; z)|^2 \exp(iq \cdot \mathbf{r}_{\parallel}). \quad (5b)$$

For illustrative purposes, take ϕ_a to be a single, optimal Gaussian,⁷

$$\phi_a(\mathbf{r}) = (2\alpha/\pi)^{3/4} \exp(-\alpha r^2), \quad (6a)$$

so from Eq. (5b),

$$\rho(q; z) = (2\alpha/\pi)^{1/2} \exp[-2\alpha(z-s)^2] \exp(-q^2/8\alpha), \quad (6b)$$

where now, the z origin is taken at the image plane, and the atom-surface separation is s . Equations (5) and (6) can be reduced⁶ to the single quadrature:

$$\delta\epsilon_a(\text{rel}) = \frac{e^2}{8} \int_0^{q_{\text{up}}} dq \left\{ e^{-qs} \left[1 - \text{erf} \left(\frac{q - 4\alpha s}{\sqrt{8\alpha}} \right) \right] + e^{qs} \left[1 - \text{erf} \left(\frac{q + 4\alpha s}{\sqrt{8\alpha}} \right) \right] \right\}^2, \quad (7)$$

with $0.5 \lesssim \delta\epsilon_a(\text{rel})/\epsilon_{\text{im}} < 1$ for atomic scale values of s and with $\epsilon_{\text{im}} = e^2/4s$, the image potential shift.⁸ As a parenthetical check, we note that the relaxation shifts experienced by the $5p$ levels of Xe physisorbed on W, as reported by Waclawski and Herbst,⁹ fall within this range.

Since a well defined procedure for calculating the adatom relaxation energy shifts [Eqs. (4)–(7)] has been given, the only remaining unknown quantity in Eq. (3) is V and thus we can conclude that (within the approximation scheme discussed here) chemisorption bonding shifts can be separated from relaxation energy shifts in photoelectron spectroscopy.

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