Self-energy of image states

A. Arnau and P. M. Echenique
Departamento de Física Facultad de Químicas, Euskal Herriko Unibersitatea, Apartado 1072, 20080 San Sebastián, Euskadi, Spain
(Received 20 November 1986)

A Coulombic basis set is used, within a self-energy formalism, to calculate the binding energy and effective-mass correction of image states at surfaces. Contributions from virtual transitions to discrete and continuous levels are evaluated separately and compared with previous calculations performed invoking the closure relationship to eliminate the sum over intermediate states.

It is well known that electrons can be trapped at surfaces by their own image potentials. Hydrogenic states of this kind were studied by Sommer,[1] Cole and Cohen,[2] and Shikin.[3] In fact the Coulombic tail of the image potential allows an infinite Rydberg-type series to exist.[4] In metals, such states can arise if a gap in the direction normal to the surface contains the vacuum level. Inverse-photoemission experiments measuring the binding energy and width of these states have been reported recently.[5–9]

Different approximations within the phase-shift-approach formalism[4,10–14] have been made to treat the problem of surface states using several models for the effective potential.[15–21]

Recent calculations by Echenique[22] and Echenique and Pendry[23] have used a many-body effective image potential within the Hedin-Lundqvist self-energy formalism,[24] with invocation of the closure relation to sum over intermediate states in the calculation of the matrix elements appearing in the definition of the many-body effective image potential.

In this paper we use a basis set of eigenfunctions of the effective potential to calculate the electron Green's function, which allows us to check the approximations involved in previous work. This is the set of Coulombic wave functions[25] for the excited states (both discrete and continuum) and a hydrogenlike variational wave function for the ground state. We can expect that the final electronic wave functions should be adequately described by such a basis set.[23] The ground-state binding energy is calculated variationally.[22,23,26] The total energy $E(\beta)$ is given by

$$E(\beta)=\frac{\beta^2}{2}-\frac{\omega_s}{2}\sum_f\int_0^\infty dQ\frac{|\langle 0|e^{-Qz}|f\rangle|^2}{\omega_s+Q^2/2+E_f-E_0}\ , \tag{1}$$

where β is the variational parameter in the ground-state wave function $|0\rangle=2\beta^{3/2}ze^{-\beta z}$, ω_s is the undispersed surface-plasmon frequency, E_f-E_0 is the energy difference between the fth excited state and the ground state associated with the normal motion, and $|f\rangle$ are the sets of eigenstates of the effective Hamiltonian associated with the normal motion, i.e., the Coulombic wave functions. In fact, E_0 is $E(\beta)$ so that we have to calculate self-consistently.

The matrix elements $\langle 0|e^{-Qz}|f\rangle$ can be calculated using the properties of the hypergeometric function,[27] for both the discrete $|n\rangle$ and the continuum states $|E\rangle$.[25] Then the sum over intermediate states is easily done and we can distinguish the contributions of the different terms in the series expansion of (1). We obtain for such matrix elements,

$$\langle 0|e^{-Qz}|n\rangle=C_0C_n\frac{2}{(\beta+Q+1/4n)^3}\left[\frac{n(\beta+Q)-\frac{1}{4}}{n(\beta+Q)+\frac{1}{4}}\right]^{n-2}\left[1-\frac{\frac{1}{4}(1+n)}{\frac{1}{4}+n(\beta+Q)}\right] \tag{2}$$

where $C_0=2\beta^{3/2}$ and $C_n=2(1/4n)^{3/2}$, so that the square of the matrix elements behaves as n^{-3} for $n\sim\infty$. For the continuum we note a well-known connection between the Coulombic bound-state and continuum wave functions, namely,

$$\frac{|n\rangle}{C_n}\leftrightarrow\frac{|E\rangle}{C_E}\quad\text{and}\quad n\leftrightarrow i\eta$$

where $\eta=1/4k$, $k=(2E)^{1/2}$, and C_E is the normalization constant of the continuum state,[25]

$$|C_E|^2=\left[\frac{\pi k}{L}\right][1-\exp(-2\pi\eta)]\ . \tag{3}$$

In Fig. 1 we plot the binding energy as a function of r_s (electron-gas density parameter) and compare it with its upper and lower bounds. We obtain the upper bound when we neglect the energy difference in the denominators of (1) and sum over intermediate states by invoking the closure relation. On the other hand, we obtain the lower bound when we take into account only the first term in the series. Different values of β minimize each binding-energy functional.

In Fig. 2 we plot the binding energy showing the contributions that arise from the different terms, namely the first term, the discrete states, and the continuum. See also Table I.

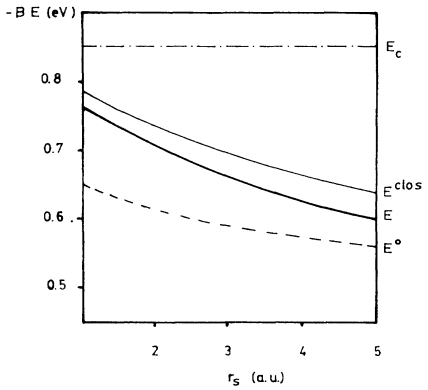

FIG. 1. Binding energy (BE) as a function of r_s obtained with the exact calculation (thick solid line), closure relation approximation (thin solid line), and using the first term in the series expansion (dashed line). See the text for the details, E_C is the Coulombic binding energy.

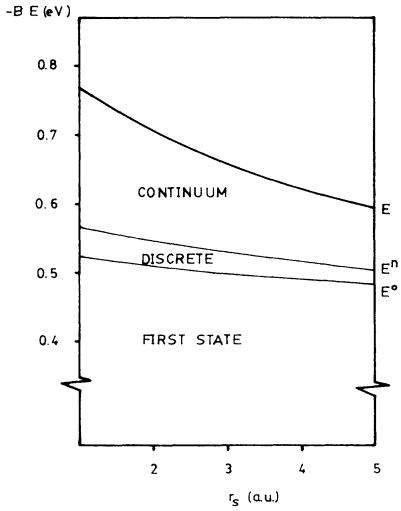

FIG. 2. Binding energy as a function of r_s showing the contributions from the different terms in the series.

TABLE I. Relative contributions to the energy shift (%).

r_s	First term	Discrete	Continuum
1	82.5	3	14.5
2	84.7	2.8	12.5
3	86.4	2.7	10.9
4	87.8	2.6	9.6
5	89	2.5	8.5

TABLE II. Effective mass corrections. δm, δm^{clos}, and δm^0 are the values obtained from the exact calculation, using closure and using only the first term in the potential energy, respectively.

r_s	δm	δm^{clos}	δm^0
1	1.2×10^{-3}	1.8×10^{-3}	4.2×10^{-4}
2	4.7×10^{-3}	7.3×10^{-3}	2.5×10^{-3}
3	9.9×10^{-3}	1.6×10^{-2}	6.8×10^{-3}
4	1.7×10^{-2}	2.6×10^{-2}	1.3×10^{-2}
5	2.5×10^{-2}	3.8×10^{-2}	2.1×10^{-2}

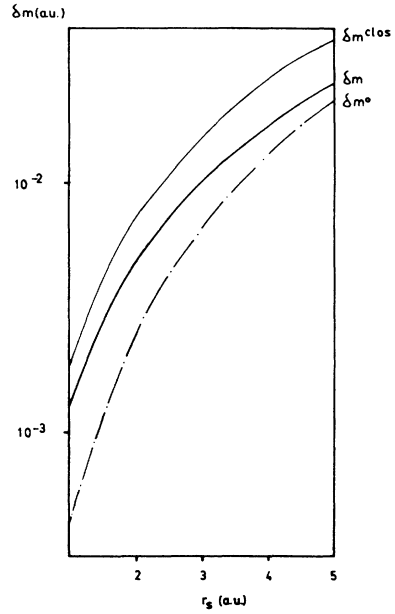

FIG. 3. Effective mass correction as a function of r_s obtained with the exact calculation (thick solid line), closure relation approximation (thin solid line), and using the first term (dotted-dashed line) of the potential energy in the calculations.

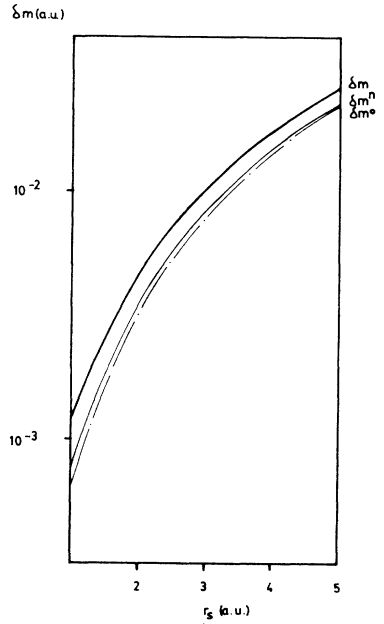

FIG. 4. Effective mass correction as a function of r_s obtained with the exact calculation showing the contributions from the different terms in the series.

TABLE III. Relative contribution to the effective mass (%).

r_s	First term	Discrete	Continuum
1	53	6	41
2	68	6	26
3	78	6	16
4	83	5	12
5	88	4	8

Figure 1 shows that to sum over intermediate states by invoking closure yields a better approximation than by taking only the first term. Figure 2 shows that the discrete contribution is almost negligible, but the continuum contribution is appreciable (10—15 %). We have also calculated the correction to the effective mass $m^* = 1 + \delta m$ where δm is obtained expanding the energy shift in powers of the parallel momentum. The results obtained are plotted in Figs. 3 and 4. We also give these results in Tables II and III. These are consistent with earlier predictions.[28–30]

We can estimate the lifetime of the first image state for high parallel momentum (k_p) from the imaginary part of the energy shift.[31] For $k_p = 2$(a.u.) we obtain 330 meV for $r_s = 2$.

In conclusion, a Coulombic basis set has been used to evaluate variationally the binding energy and effective mass of image states at metal surfaces. Contributions arising from virtual transitions to discrete and continuum states have been evaluated. Our calculation quantitatively confirms the validity of the use of the closure approximation by previous workers, especially for the binding energy.

ACKNOWLEDGMENTS

We thank the Spanish Comisión Asesora and Diputación de Guipuzcoa for partial financial support. One of us (P.M.E.) gratefully acknowledges help and support from Iberduero Sociedad Anonima. This work was sponsored in part by a grant from the United States—Spain Joint Committee for Scientific and Technological Cooperation.

[1]W. T. Sommer, Ph.D. thesis, Stanford University, 1964.
[2]M. Cole and M. H. Cohen, Phys. Rev. Lett. **23**, 1238 (1969).
[3]V. B. Shikin, Zh. Eksp. Teor. Fiz. **58**, 1748 (1970) [Sov. Phys.—JETP **31**, 936 (1970)].
[4]P. M. Echenique and J. B. Pendry, J. Phys. C **11**, 2065 (1978).
[5]S. L. Hulbert, P. D. Johnson, and W. Weinert, Phys. Rev. B **34**, 3670 (1986).
[6]W. Altman, V. Dose, A. Goldmann, C. Kolac, and J. Rogozik, Phys. Rev. B **29**, 3015 (1984).
[7]D. Straub and F. J. Himpsel, Phys. Rev. Lett. **52**, 1922 (1984).
[8]B. Reihl, K. H. Frank, and R. R. Schlittler, Phys. Rev. B **30**, 7328 (1984).
[9]D. F. Woodruff, S. L. Hulbert, P. D. Johnson, and N. V. Smith, Phys. Rev. B **31**, 4046 (1985).
[10]P. M. Echenique, Ph.D. thesis, Cambridge, 1976.
[11]K. Giesen, F. Hage, F. J. Himpsel, H. J. Riess, and W. Steinmann, Phys. Rev. B **33**, 5241 (1986).
[12]E. G. McRae, Rev. Mod. Phys. **51**, 541 (1979).
[13]M. Ortuño and P. M. Echenique, Phys. Rev. B **34**, 5199 (1986).
[14]M. Weinert, S. L. Hulbert, and P. D. Johnson, Phys. Rev. Lett. **55**, 2055 (1985).
[15]D. Straub and F. J. Himpsel, Phys. Rev. B **33**, 2256 (1986).
[16]A. Goldmann, V. Dose, and G. Borstel, Phys. Rev. B **32**, 1971 (1985).
[17]A. Goldmann, M. Donath, W. Altmann, and V. Dose, Phys. Rev. B **32**, 837 (1985).
[18]N. V. Smith, Phys. Rev. B **32**, 3549 (1985).
[19]N. V. Smith, Appl. Surf. Sci. **22/23**, 349 (1985).
[20]S. L. Hulbert, P. D. Johnson, N. G. Stoffel, W. A. Royer, and N. V. Smith, Phys. Rev. B **31**, 6815 (1985).
[21]S. L. Hulbert, P. D. Johnson, N. G. Stoffel, and N. V. Smith, Phys. Rev. B **32**, 3451 (1985).
[22]P. M. Echenique, J. Phys. C **18**, L1133 (1985).
[23]P. M. Echenique and J. B. Pendry, J. Phys. C **19**, 5437 (1986).
[24]L. Hedin and S. Lundqvist, Solid State Phys. **23**, 1 (1969).
[25]R. Shakeshaft and L. Spruch, Phys. Rev. A **31**, 1535 (1985).
[26]R. M. Nieminen and C. H. Hodges, Phys. Rev. B **18**, 2568 (1978).
[27]L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory, Third Edition* (Pergamon, Oxford, 1977).
[28]J. Bausells, P. M. Echenique, and F. Flores, Surf. Sci. **178**, 268 (1986).
[29]P. M. Echenique and J. B. Pendry, Surf. Sci. **166**, 69 (1986).
[30]J. B. Pendry, C. G. Larsson, and P. M. Echenique, Surf. Sci. **166**, 57 (1986).
[31]P. M. Echenique, F. Flores, and F. Sols, Phys. Rev. Lett. **55**, 2348 (1985).