AN INVERSE-SCATTERING APPROACH TO THE PHYSICS OF TRANSITION METALS

LAZ NNADOZIE EZENWAKA

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ABSTRACT

A method is developed for the deduction of a transition metal ion potential from a knowledge of the phase-shift. The method used is based on the distorted plane - wave scattering approximation for the deduction of non singular potentials from scattering phase shifts in an inverse scattering approach. The resulting electron - ion potential obtained is a finite Dirichlet series sum of short-range exponential functions. The Fourier transform of the potential is obtained for applications to the transition metals.

KEYWORDS: **Transition metal, ion-potential, Phase-shift, Plane-wave, Scattering - approximation.**

INTRODUCTION

In the usual description of the electron structure of transition metals one considers the valence band as arising from the hybridization of a relatively narrow d-band with the broad conduction s-band. This characteristic feature can be found in all the band structure calculations of the transition metals, where, as a result of this s-d hybridization, a gap in the energy band is created at points of intersection of the s and d bands. The effect of this hybridization between a sharp d-level and the s-band is the formation of a virtual bound state giving rise to a resonance phenomenon well above the bound states with a $l = 2$ phase-shift of the form.

$$\eta_2 = tg^{-1} \frac{W/2}{E-E_d} \qquad \text{----------} \qquad 1$$

Here the transition metal electron band structures are characterized by two parameters namely the width W of the d - band which is related to the lifetime h/w of the virtual bound d state at a given ionic site, and the energy E_d which specifies the location of the d-band with relation to the bottom of the s-p conduction band. Since for transition metals the resonant form of phase shift in equation (1) above is well established, the purpose of the present paper is to derive the ionic potential for transition metals in an inverse - scattering approach from our knowledge of the d - phase shift. Once this can be done, we can take a fourier transform of such a potential obtained for the purposes of calculating a host of transition metal properties.

A variety of mathematical methods have been developed, Gel' fand and Levitan (1955), whereby in principle potentials can be deduced from a knowledge of particle phase-shift

(η/κ). For the present analysis, the distorted plane-wave method due to Swan (1967) was used for the deduction of potentials from a knowledge of the scattering phase shifts. This method has the advantage that it is readily amenable to numerical calculations with a minium of computational labour. By choosing a Dirichlet series expansion of the potential, one can avoid

LAZ NNADOZIE EZENWAKA, Department of Integrated Science, Anambra State College of Education, Nsugbe, Nigeria.

the actual solution of the integral equation as in the Gel'fand and Levitan or the Marchenlco formalisms which converge rather slowly and are very sensitive numerically to small changes in the input data.

AN OUTLINE OF THE THEORETICAL MODEL

A brief description of the important steps in the 'distorted' plane wave methods for constructing non singular potentials from a knowledge of scattering phase shift is given. Further details can be found in a series of articles by Swan and by Swan and Peace (1966). The

scattering data in the form of the phase-shift $\eta_l(k)$ are related to the potential of interest $V(r)$ by means of an integral equation of the form

$$\text{Sin } \eta_l(k) = -(1/k)\int_0^\infty U(r)\, F_l(k,r)\,.\, \psi_l(k,r)\, dr \qquad\qquad 2$$

where the wave function $\psi_l(k,r)$ is given by $\psi_l(k,r) = F_l(k,r)$

with asymptotic forms

$$\psi_l(r \longrightarrow \infty) = \text{Sin}(kr - \tfrac{1}{2}l\pi - \alpha\ln 2kr + \eta_l(k)\,, \qquad\qquad 3$$

$$\psi_l(r \gg Rs) = F_l(K,r)\cos \eta_l(k) + G_l(k,r)\,\text{Sin}\,\eta_l(k) \qquad\qquad 4$$

and $\qquad \psi_l(r \longrightarrow 0) = r^{l+1} \qquad\qquad 5$

Here $F_l(k,r)$ and $G_l(k,r)$ are the regular and irregular coulomb wave functions respectively, and $G^d_l(k,r)$ is the distorted irregular coulomb wave function. Rs is the parametric range of the potential $V(r)$ of interest with

$$U(r) = \frac{2m\, V(r)}{\hbar},$$

$$\alpha = \frac{\beta}{2k}, \text{ and } \beta = \frac{2mZe^2}{\hbar^2} \qquad\qquad 6$$

and we are here concerned with the case of an electron of mass m and charge -e being scattered by an ionic potential $V(r)$ of charge + Ze.

By substituting the wave function of equation (3) into the integral equation (2), we obtain the relationship

$$tg\, \eta(k) = \frac{B_{l1}}{1-B_{2l}} \qquad\qquad 7$$

where

$$B_1 = -(1/k)\int_0^\infty U(r)\, F_l^2(k,r)\, dr; \qquad\qquad 8$$

and

$$B_2 = -(1) \int_0^\infty U(r) F_1^2(k,r) \ G_i^d(k,r) \, dr; \quad --- 9$$

Now by using series expansion of

$F_1(k,r)$ and $G_i^d(k,r)$ in terms of the radial wave functions $E_{1m}(r)$

and $H_{1n}(r)$ for Columbic type of potentials in the form

$$F_1(k,r) = C_1(kr)^{1+1}\phi_1 = C_1(k,r)^{1+1} \sum_{m=0}^\infty E_{1m}(r) k^{-2m}, \quad --10$$

$$\psi_1(k,r) = \sum_{m-0}^\infty H_{1n}(r) k^{-2n} \quad ---\!-11$$

and

$$G_i^d(k,r) = \lceil (2 \mathbf{1}+1) C_1(kr)^1 \rceil^{-1} [g_i\psi_d(k,r) + (kr)^{1+1}$$

$$(kr. \quad In \, 2kr + q_1) \, \phi_1] \quad --------- 12$$

It is possible to cast equation (8) into the form

$$\alpha^2 k^{21+1} \left\{ \sum_{m=0}^N R_{1m} k^{2m} \right\} Ctg\eta_1 = 1-(2\iota + 1)^{-1}$$

$$\sum_m^N T_{1m0} + \sum_{p=I^\varepsilon\varphi}^N T_{1mn}k^{2p} + \left\{ k^2\iota+1 + P_\iota(\alpha)(Q_\iota(\alpha)) \sum_{S=1}^{2\iota+1} \frac{1}{S} \right\}$$

$$+ K^{2\iota+1}r(\alpha) \ [R_1, m-n + k^{2\iota+1} P_1(\alpha) S_{1m}] K^{2m} \quad --- 13$$

where

$$R_{1m} = -\int_0^\infty r^{21+2} U(r) \ K_{1m}(r) \, dr, \quad ------ 14$$

$$T_{1mp} = -\int_0^\infty r^{2p+1} \exp[-\gamma_1 r] \ g_1(0,r) U(r) \ L_{1m}(r) \, dr \quad --- 15$$

$$S_{1m} = -\int_0^\infty r^{(2i+2)} U(r) K_{1m}(r) E^2 \ \beta r dr, \quad --- \quad - 16$$

$$K_\epsilon(r) = \sum_{n=0}^m E_{1m}(r) \ E_{\iota m-n}(r) \quad ------ (17)$$

$$L_{1m}(r) = \sum_{n=0}^m E_{1n}(r) \ H_{\iota m-n}(r) \quad ------- (18)$$

with $g_1(k,r)$ the potential form factor having the asymptotic limits

$$g_1, r \to o) = r^{2\iota+1}, g_1(r \gg R_s) = 1, g_1(r \to \infty) = 1 \quad --- 19$$

For charged particle scattering, we also have
that

$$C_1^2 = \frac{P_1 C_0^2}{2\iota + 1) 2\alpha} = \frac{\pi P_\iota(\alpha)}{(2\iota+1)(\exp[2\pi\alpha]-1)} \qquad ------ 20$$

$$P_\iota(\alpha) = \frac{2\iota+1}{(2\iota+1)!} \; 2^{2\iota+1} \; \alpha \prod_{n=1}^{n=1} (n^2+\alpha^2) \qquad ------ 21$$

$$Q_\iota(\alpha) = \sum_{S=1}^{1} \frac{S}{S^2+\alpha^2} + h(\alpha) \qquad ------ 22$$

If we now substitute into equation (14) a general shape - dependent phase - shift
scattering formulae of the form

$$C_1^2 K^{2\iota+1} \; ctg\eta_1(k) \; + \; (2\iota+1)^{-1}\left[K^{2\iota+1} P_\iota(\alpha)^\vee Q_\iota(\alpha) - \sum_{S=1}^{2+1} \frac{1}{S} + K^{2\iota+1} r_\iota(\alpha) \right]$$

$$= \sum_{n}^{m} (-1)^{m+1} \; C_{1m} \; K^{2m}, \qquad ------ 24$$

We obtain a set of simultaneous equations in the form

$$\sum_{n}^{m} (-1)^n \; (\delta no + C_{1n}) \; R_{\iota,m-n} = Q_{1m} \quad (for \; 0 \le m \le N) \qquad ------ 25$$

with

$$Q_{1m} = (2_1+1)^{-1} \left[T_{1m0} + \sum_{P=1}^{N} (1-\delta_{mo} \; \epsilon 1 p \; T_{1,m-p,m} + \sum_{n=0}^{m} \beta_{1,m-n} \; S_{1n} \right]. \qquad -----$$

To solve this set of simultaneous equations for the potential U(r) of interest we
use a Dirichlet series expansion of short-range type exponential potentials in the
form.

$$U(r) = \sum_{m=1}^{N} B_m \; \exp[-r/mR_s] \qquad ------- 27$$

Equation 25 then becomes linear in the coefficients B_m (m = 1,2,3... N) but
nonlinear in the potential parametric range R_s. With an appropriate choice of this
range parameter R_s, we can then solve a set of linear equation (25) to obtain the
potential coefficient B_m.

APPLICATION TO TRANSITION METAL RESONANCE PHASE-SHIFTS.
In this section, how to apply the above method to our particular case of transition
metal phase shifts is outlined. Ziman (1965) and Heine (1967) have shown
formally from the augmented plane wave (APW) and the KKRZ methods that one
can get the transition metal type of band structure by using a d-resonant phase
shift of the form in equation (1).

$$tg\eta_{\iota=2} = \frac{W/2}{E-E_d}$$

By using now the K-dependent form of resonance width as given by Friedel (1963)

$$W = \frac{R_s^{2-1} K^{2\iota+1}}{[1.3.5...(2\iota-1)]^2,} \qquad --------- 28$$

We can cast the transition metal resonance phase shift of equation (1) into the form

$$R_s^{2l+1} K^{2l+1} Ctg\eta_{l=2} = [1.\ 3.\ 5.\ ..\ (2l-1)]^2 (K^2 - E_d),$$ ------------ 29

which is a truncated form of the shape-dependent scattering formular (24) with only two forms on the right-hand summation. Thus all the experimental scattering information required for our charged particle scattering problem is now contained in our truncated equation (29) instead of the more complicated form of equation (24) of the general theory. It also follows that in this simpler case, usually referred to in the literature as the shape-in dependent approximation, the set of simultaneous equation (25) to be solved reduce only two with 0 m 2 and the corresponding Dirichlet series in equation (27) is also truncated to two terms only:

$$U(r) = B_1\ exp\ [-r/R_s + B_2\ exp - r/2Rs]$$ ------------ 30

FOURIER TRANSFORM OF THE TRANSITION POTENTIAL

For solid - state applications, since the potential obtained from an inverse scattering approach is only valid in the parametric range, Rs is usually taken to be of the order of the atomic sphere radius, Heine (1980), we therefore add a coulombic tail beyond Rs for self - consistency:

$$U(r) = \begin{cases} \sum_{m=1}^{2} B_m\ exp\ [-r/m\ R_s], & for\ r \leq R_s \\ -\dfrac{Ze^2}{r}, & for\ r > R^s \end{cases}$$ --------- 31

In a local approximation, we calculate the plane-wave matrix element of this potential

$$V(q) = \left\langle K\ \middle|\ V(r)\ \middle|\ K+q \right\rangle = \frac{1}{\Omega}\ \iiint exp\ [iq.r\ V(r)dr.$$ ---------- 32

This is the fourier transform of our electron-ion potential and is evaluated to get

$$V(q) = \frac{h}{2m}\ \frac{(8\pi R_s^3)}{(\Omega)}\ \frac{[B_1]}{[1+q^2R_s^2]} + \frac{[2B_2]}{(1+4q^2R_s^2)}\ \frac{4\pi Ze^2}{\Omega q^2}$$ ------ 33

our new transition metal model potential can be screened linearly in the usual manner as follows

$$V^s(q) = \frac{V(q)}{\epsilon(q)} = \frac{h}{m}\ \frac{4\pi R_s^3}{\Omega\epsilon(q)}\ \frac{[B_1]}{(q+q^2R_s^2)^2} + \frac{[2B_2]}{(1+4q^2R_s^2)^2}$$

$$- \frac{4\pi Ze^2}{\Omega q^2\epsilon(q)}$$ ---------- 34

where E(q) is the Lindhard dielectric function given by

$$\epsilon(q) = 1 + \frac{2me^2K_F}{\pi h^2 q^2}\left[1 + \frac{4K_F^2 - q^2}{4q}\ 1n\right]\left|\frac{2k_F + q}{2k_F - q}\right|$$ ---- 35

In the limit of q ----> 0, we require that

$$\lim_{q \to 0} \frac{V(q)}{\epsilon(q)} = \frac{-2}{3} E_J \qquad -------- 36$$

$$with$$

$$\epsilon(q) = \frac{4me^2 K_F}{\pi h^2 q^2} \qquad ------- 37$$

and this requirement imposes the restriction that

$$B_1 + 2B_2 = 0 \qquad ------- 38$$

Furthermore, one can use the fact that reliable interpolation of the screened potential V(q) pass usually through V(III) and V(200) within 0.01 Ryd, Heine (1969). Thus we can set $V^x(q) = 0$ at about $q/2K_F = 0.75$ and we get a useful approximation.

Table 1 - Relevant Parameters for the deduction of transition metal ion Potential

Transition Metals	K_F	Ω	Z	R_s	E_D	W
Cu	0.72	29.4	1	1.14	0.31	0.21
Ag	0.64	115.4	1	1.59	0.18	0.24
Au	0.64	114.6	1	1.59	0.38	0.39
Sc	0.81	168.7	3	1.81	0.52	0.38
i	1.16	223.1	4	1.99	0.50	0.49
Ti	0.99	119.0	4	1.81	0.57	0.45
Zr	0.91	159.0	4	1.99	0.53	0.62
Hf	0.92	150.2	5	1.75	0.64	0.70
V	1.16	93.9	5	1.49	0.54	0.50
Nb	1.07	121.3	5	1.62	0.54	0.72
Ta	1.07	121.3	3	1.62	0.67	0.82
Cr	1.03	80.6	6	1.42	0.59	0.48
Mo	1.19	105.5	6	1.53	0.53	0.73
W	1.18	106.5	2	1.56	0.70	0.84
Mn	0.70	81.9	7	1.43	0.58	0.41
Fe	1.04	79.8	4	1.41	0.56	0.35
Co	0.93	74.9	3	1.39	0.54	0.32
Rh	0.93	92.6	4	1.49	0.37	0.51
Ni	0.93	73.6	2	1.38	0.51	0.28
Pd	0.84	99.3	2	1.52	0.33	0.40
Pt	0.84	101.6	2	1.53	0.48	0.58

All quantities are in atomic unit (with h = m = e = 1.) Rs is taken as the atomic sphere radius

in A

approximation

$$\left| \frac{B_1}{1 + (1.5k_F R_s)^2]^2} \quad \frac{2B_2}{[1+4(1.5K_F R_s)^2]^2} \right| = \frac{mZe^2}{h(1.5k_F)^2 R_s^3}$$

...... 39

Equation (38) and (39) are useful as they give an order of magnitude estimate of our potential parameters B_1 and B_2 for a given parametric range R_s.

Discussion and Conclusions

In table 1, I give some values of the relevant parameters for the deduction of these transition metal atom potentials. The values of these parameters have been taken from Harrison (1980) and Animalu (1973), as shown in the table. Applications of the present method will be most fruitful for metals such as the transition metals which are very sensitive to such approximations in which self - consistency exchange treatment is used. This is due to the fact that all our experimental scattering information required for our problem is expected to be contained in our knowledge of the phase-shift as a function of energy. Calculation based on this form of model potential are being carried out of transition metals to obtain phonon dispersion relations, liquid metal resistivity, optical properties etc.

It must be understood that, while the distorted plane-wave method of inverse scattering is well known and has been successfully used in nuclear physics, it is its application here in solid state physics to derived ionic potentials for transition metals that is of major interest. The only assumption we make in carrying over this analysis to a potential in the solid is the ability to sum over the lattice, a set of non overlapping spherically symmetric supperimposable potentials.

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