MULTIPLE SCATTERING Xα TREATMENT OF SCATTERING STATES OF CLUSTERS

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The multiple scattering Xα method seems to be an appropriate tool to handle scattering states of clusters. We formulate the solution of the scattering problem in the language used by Johnson to determine bound states of clusters.

The Xα potential approximation combined with the multiple scattering method has turned out to be a very effective and successful computational scheme in determining bound states of polyatomic molecules [1]. JOHN and ZISCHE [2, 3] have shown how to treat scattering states of clusters by this multiple scattering (MS) method, but the equations they derived can be applied only for potentials constant outside the — not necessarily spherically symmetric — muffin tin regions (no Watson sphere). This restriction, however, can be removed as DILL and DEHMER and ZIESCHE have recently pointed out [4, 5]. We want to show in this paper, that with a slight modification of the existing computer programs [6] phase shifts of clusters with Watson sphere can be determined. Note that the method of JOHNSON and that of JOHN and ZIESCHE are equivalent.

First we summarize the MS method in the muffin tin approximation [1]. The space is partitioned into regions of three types:

(I) Atomic region, consisting of atomic spheres containing an atomic nucleus at their center $\vec{R}_p$ $(p=1, 2, ..., N)$. In the p-th atomic sphere of radius b_p the potential V_p is taken to be spherically symmetric.

(III) Outer region, defined by $|\vec{r}-\vec{R}_0| \geqq b_0$, where b_0 is the radius of the so called Watson sphere containing the atomic region and centered at $\vec{R}_0$. The potential V_0 in this region is spherically symmetric.

(II) Interatomic region, bounded by regions (I) and (III). In this region the volume averaged potential is $\bar{V}$.

The one-electron wave functions of the cluster are the solutions of the Schrödinger equation

$$[\Delta + k^2 - V(\vec{r})]\psi = 0 \tag{1}$$

where $k^2 = E$ and $V(\vec{r})$ is the spherically or volume averaged cluster potential.

Within the p-th atomic sphere the solution can be expanded into partial waves

$$\psi^p(\vec{r}_p) = \sum_L C_L^p R_l^p(k; r_p) Y_L(\hat{r}_p) \qquad (0 \leqq r_p \leqq b_p) \tag{2}$$

where $\vec{r}_p = \vec{r} - \vec{R}_p$, $L \equiv (l, m)$ and the functions R_l^p are solutions of the radial equation

$$\left[-\frac{1}{r^2}\frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{r^2} + V^p(r) - k^2\right] R_l^p(k; r) = 0 \tag{3}$$

These solutions can be obtained by outward numerical integration as they must be regular at the center $r=0$. In the outer region the cluster wave functions can be written in the form

$$\psi^0(\vec{r}_0) = \sum_L D_L^0 R_l^0(k; r_0) Y_L(\hat{r}_0) \qquad (b_0 \leqq r_0) \tag{4}$$

where $\vec{r}_0 = \vec{r} - \vec{R}_0$, and the functions R_l^0 satisfy the radial equation (3), but with $V_0(r)$ instead of $V_p(r)$. For bound states the functions R_l^0 must decay exponentially at large distances, so that R_l^0 can be generated by inward numerical integration.

In the interatomic region we can write the solution of Eq(1) in the form

$$\psi_{II}(\vec{r}) = \sum_p \sum_L A_L^p F_l(\varkappa r_p) Y_L(\hat{r}_p) + \sum_L B_L^0 J_l(\varkappa r_0) Y_L(\hat{r}_0) \tag{5}$$

where $\varkappa = \sqrt{|E - \overline{V}|}$ and

$$F_l = \begin{cases} k_l^1, & E < \overline{V} \\ n_l, & E > \overline{V} \end{cases}; \qquad J_l = \begin{cases} i_l, & E < \overline{V} \\ j_l, & E > \overline{V} \end{cases} \tag{6}$$

(Here we have used Bessel functions j_l, n_l, i_l, k_l^1, as they were used in [1].)

Requiring the continuity of the wave functions and their first derivatives, we are led to a system of linear homogeneous equations [1]:

$$\begin{aligned} \sum_{p'} \sum_{L'} [T^{-1}(E)]_{LL'}^{pp'} A_{L'}^{p'} + \sum_{L'} S_{LL'}^{p0}(E) B_{L'}^0 &= 0 \\ \sum_{p'} \sum_{L'} S_{LL'}^{0p'} A_{L'}^{p'} + \sum_{L'} \delta_{LL'} [g_l^0(E)^{-1}] B_{L'}^0 &= 0 \end{aligned} \tag{7}$$

in which $[T^{-1}(E)]_{LL'}^{pp'} = \delta_{pp'} \delta_{LL'} [t_l^p(E)]^{-1} + (1 - \delta_{pp'}) G_{LL'}^{pp'}(E)$

$$g_l^0(E) = \frac{[F_l, R_l^0]_{b_p}}{[J_l, R_l^0]_{b_0}} \qquad t_l^p(E) = \frac{[J_l, R_l^p]_{b_p}}{[F_l, R_l^p]_{b_p}};$$

$$G_{LL'}^{pp'}(E) = 4\pi \sum_{L''} s(L'', L, L'; E) I_{L''}(L, L') F_{l''}(\varkappa R_{pp'}) Y_{L''}(\hat{R}_{pp'})$$

$$S_{LL'}^{p0}(E) = 4\pi \sum_{L''} s(L'', L, L'; E) I_{L''}(L, L') J_{l''}(\varkappa R_{p0}) Y_{L''}(\hat{R}_{p0})$$

Here
$$s(L'', L, L';\ E) = \begin{cases} (-1)^{l+l'}, & E < \overline{V} \\ i^{l-l'-l''}, & E > \overline{V} \end{cases}$$

$$[J_l, R_l^p]_{b_p} = \left(J_l(\varkappa r) \frac{dR_l^p}{dr} - R_l^p \frac{dJ_l(\varkappa r)}{dr} \right)_{r=b_p}$$

$$\vec{R}_{pp'} = \vec{R}_{p'} - \vec{R}_p; \qquad \vec{R}_{po} = \vec{R}_o - \vec{R}_p$$

and $I_{L''}(L; L')$ are the Gaunt integrals. The continuity requires also

$$\begin{aligned} C_L^p &= (\varkappa b_p^2 \sigma_l(E)[J_l, R_l^p]_{b_p})^{-1} A_L^p \\ D_L^0 &= (-\varkappa b_0^2 \sigma_l(E)[F_l, R_l^0]_{b_0})^{-1} B_L^0 ; \end{aligned} \qquad \sigma_l(E) = \begin{cases} (-1)^{l+1}, & E < \overline{V} \\ 1, & E > \overline{V} \end{cases} \tag{8}$$

These equations have been programmed and used very efficiently in SCF calculations treating localized electronic charge distribution of clusters [1].

In the case of scattering states ($E>0$), the only difference is in the boundary conditions satisfied by the functions R_l^0 at large distances. If the potential $V_0(r_0)$ tends to zero sufficiently rapidly as r_0 tends to infinity, or, to be more definite, V_0 vanishes outside a sphere of radius R

$$V_0(r_0) = 0 \qquad r_0 > R > b_0.$$

DEMKOV and RUDAKOV [7] have shown, that the asymptotic behaviour of the solution of Eq. (1) can be characterised by the formula

$$\psi(r \to \infty) \sim \sum_L D_L^0 [j_l(kr_0) - \operatorname{tg} \delta n_l(k_{r0})] \psi_L(\hat{r}_0), \tag{9}$$

where δ is the phase shift of the cluster. It can be seen, that the appropriate solution of the radial equation (3) in region $r_0 \geqq R$ is

$$R_l^0(r_0) = j_l(kr_0) - \operatorname{tg} \delta\ n_l(kr_0), \tag{10}$$

and in region $b_0 \leqq r \leqq R$

$$R_l^0(r_0) = u_l(r_0) - \operatorname{tg} \delta\ v_l(r_0) \qquad b_0 \leqq r_0 \leqq R, \tag{11}$$

where $u_l(r)$ and $v_l(r)$ are determined by inward numerical integration with the following starting values at $r_0 = R$:

$$u_l(R) = j_l(kR), \qquad v_l(R) = n_l(kR),$$

$$\frac{du_l}{dr}(R) = \frac{dj(kR)}{dr}\bigg|_{r=R}, \qquad \frac{dv_l}{dr}(R) = \frac{dn_l(kr)}{dr}\bigg|_{r=R}.$$

Because the phase shift δ enters Eq. (7) via

$$g_l^0(E, \delta) = \frac{[n_l(\varkappa r), R_l^0]_{b_0}}{[j_l(\varkappa r), R_l^0]_{b_0}} = \frac{[n_l, u_l]_{b_0} - \operatorname{tg} \delta [n_l, v_l]_{b_0}}{[j_l, u_l]_{b_0} - \operatorname{tg} \delta [j_l, v_l]_{b_0}}, \tag{12}$$

the secular determinant with constant energy E will not be zero except at certain values δ_λ of the phase shift. So we obtain a set of solutions $\{A_{l\lambda}^p, B_{l\lambda}^0\}_\lambda$ corresponding to δ_λ. In this way the solutions ψ_λ of Eq. (1) can be obtained. Knowing the eigen

phase shifts δ_λ and amplitudes $D^0_{i\lambda}$ we can express, for example, the scattering amplitude of the cluster [7]:

$$f(\hat{k}, k') = \frac{4\pi}{2i} \sum_\lambda (e^{2i\delta_\lambda} - 1) A^*_\lambda(k)(k'),$$

where

$$A_\lambda(\hat{k}) = \frac{1}{\cos \delta_\lambda} \sum_L (-i)^l D^0_{L\lambda} Y_L(\hat{k})$$

We hope that the little modification of existing computer programs needed to get phase shifts δ_λ, allows to treat with this method physical problems in which scattering states are of importance.

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ИССЛЕДОВАНИЕ СВОБОДНЫХ СОСТОЯНИЙ КЛАСТЕРОВ МЕТОДОМ МНОГОКРАТНОГО РАССЕЯНИЯ

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Метод многократного рассеяния вместе с методом X_α представляется пригодным для исследования свободных состояний кластеров. Мы сформулировали проблемы рассеяния на языке примененным Джонсоном для определения связанных состояний кластеров.