

Empirical tests of the electron-atom dispersion relation

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Received 29 January 1976, in final form 28 April 1976

Abstract. Recent experimental results are used to test the dispersion relation for electron scattering by hydrogen, helium and neon. Calculations of the H^- residue and of the Born exchange term for helium are reported. The sum rule appears to fail for electron, but not for positron, scattering. The nature of the singularities in the exchange amplitude is discussed.

1. Introduction

It is well known that a forward dispersion relation holds for a wide class of potential scattering problems. Gerjuoy (1958) suggested that provided the many-body Green's function had certain (reasonable) analytic properties a similar relation would hold for electron-atom scattering. Together with Krall (Gerjuoy and Krall 1960, 1962) he applied it to the analysis of available experimental data on scattering by hydrogen and helium atoms. They concluded that one of two total cross section measurements in hydrogen was to be preferred.

In recent years Bransden and McDowell have applied phaseshift analysis of experimental measurements to test the consistency of the dispersion relation for scattering by the rare gases. They concluded (Bransden and McDowell 1969, McDowell 1971a, b, 1974, Naccache and McDowell 1974, Bransden 1976) that within the accuracy of the then current data it was satisfied for electron-helium elastic scattering below the first inelastic threshold.

Bransden and Hutt (1975) analysed positron-helium total cross section measurements and concluded that the zero-energy form of the dispersion relation (which takes the form of a sum rule and is discussed further below) was well satisfied, and was also satisfied for positron-neon scattering.

This work was one of the factors which stimulated the interest of experimental physicists in obtaining accurate absolute measurements of elastic differential cross sections and of total cross sections for the rare gases and other simple systems. Such absolute measurements are dependent on the use of the phaseshift analysis technique both at a resonance (Gibson and Dolder 1969) and elsewhere (Williams 1975, 1976). In particular, de Heer re-measured the differential elastic cross section

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for electrons on the rare gases at energies above 100 eV (Normand 1930, Jansen *et al* 1976) and combined these results with the available data on excitation and ionization to derive total cross sections (see also de Heer 1976). The corrections to Normand's data were large, as suggested by Inokuti and McDowell (1974). Analysis of the new data suggested to us that the sum rule might not hold for electron-helium scattering. This conclusion motivated a more detailed investigation which is reported here.

Other workers (Byron *et al* 1975, Burke and Blum 1976) reached the same conclusion independently and their work is discussed below. The existence of a left-hand cut in the region of analyticity of the elastic scattering amplitude $f(\theta, k^2)$ in the complex k^2 plane demonstrated for the short-range force, three-body problem by Rubin *et al* (1967) is not in itself a conclusive reason for supposing that the dispersion relation, as usually written, is incorrect.

We investigate electron scattering by hydrogen, helium, lithium and neon. In §2 we summarize the dispersion relations and in succeeding sections (§3–§6) discuss each system in turn. Our conclusions are summarized in §7.

2. The Gerjuoy–Krall dispersion relation

Let $f(\theta, k^2)$ be the complex elastic scattering amplitude at angle θ and energy k^2 Ryd and $f_B(\theta, k^2)$ the first Born approximation to it, including exchange. Gerjuoy and Krall (1960) showed that with reasonable assumptions about the analytic structure of the full Green's function a dispersion relation could be written for the function

$$Q(\theta, k^2) = f(\theta, k^2) - f_B(\theta, k^2). \quad (1)$$

Making use of the optical theorem

$$\text{Im} f(0, k^2) = \frac{1}{4} k \sigma(k^2) \quad (2)$$

where σ is the total cross section (in πa_0^2), this takes the form, for electron scattering by the rare gases and in the forward direction,

$$\text{Re} f(0, k^2) = f_B(0, k^2) + \frac{P}{4\pi} \int_0^\infty \frac{k' \sigma(k'^2) dk'^2}{k'^2 - k^2}. \quad (3)$$

We have assumed that the rare gases have no bound negative-ion states accessible by electron impact from the ground state (e.g. $\text{He}^- 1s2s2p\ ^4P_{5/2}$) and that resonance poles lie on the second sheet.

Here

$$f_B(\theta, k^2) = f_B^D(\theta, k^2) - f_B^E(\theta, k^2) \quad (4)$$

is split into a direct (f_B^D) and exchange (f_B^E) contribution.

For scattering by atomic hydrogen there are two spin channels, and Gerjuoy and Krall (1960) obtain

$$\text{Re} f^\pm(0, k^2) = f_B^\pm(0, k^2) + \frac{P}{4\pi} \int_0^\infty \frac{\sigma^{(\pm)}(k'^2) k' dk'^2}{k'^2 - k^2} - \frac{1}{2} \bar{R} \delta_{S,0} \quad (5)$$

where (+) indicates singlet and (−) triplet scattering having $S = 0$ and $S = 1$ respectively.

$$f^\pm = f^D \pm f^E \quad (6)$$

and \bar{R} is the residue of $Q^+(0, E')(E' - E)^{-1}$ at the singlet bound-state energy of $H^-((1s)^2\ ^1S_0)$.

Taking

$$\sigma = \frac{3}{4}\sigma^{(-)} + \frac{1}{4}\sigma^{(+)} \quad (7)$$

as the total cross section we have for $\theta = 0$

$$\text{Re}(f^D - \frac{1}{2}f^E) = (f_B^D - \frac{1}{2}f_B^E) + \frac{P}{4\pi} \int_0^\infty \frac{k'\sigma(k'^2) dk'^2}{k'^2 - k^2} - \frac{1}{2}\bar{R} \quad (8)$$

and

$$\bar{R} = \frac{R}{k^2 + |\epsilon(H^-)|} = \tilde{R}(k^2). \quad (9)$$

The relation takes the same form for electron-lithium scattering if a single singlet bound state is assumed.

The forward Born direct amplitude $f_B^D(0, k^2)$ is independent of energy, so on subtracting the zero-energy dispersion relation we have for (3)

$$\text{Re} f(0, k^2) + A = f_B^E(0, 0) - f_B^E(0, k^2) + \frac{k^2 P}{4\pi} \int_0^\infty \frac{\sigma(k'^2) dk'^2}{k'(k'^2 - k^2)}. \quad (3')$$

Both (3) and (3') should give identical results for $\text{Re} f(0, k^2)$, if they are true, provided the correct values of the scattering length A , Born exchange amplitude $f_B^E(0, k^2)$ and the total cross section at all energies are used.

A similar relation exists for hydrogen, and we define

$$\tilde{A} = \frac{1}{4}(a^+ + 3a^-) \quad (10)$$

where $a^{+, -}$ are the singlet and triplet scattering lengths.

In the zero-energy limit,

$$\text{Re} f(0, k^2) \xrightarrow{k^2 \rightarrow 0} -A$$

and the dispersion relations (3) and (8) take a simple sum-rule form not involving a principal value:

$$-A + f_B^E - f_B^D = \frac{1}{2\pi} \int_0^\infty \sigma(k'^2) dk' \quad (3'')$$

$$-\tilde{A} + (\frac{1}{2}f_B^E - f_B^D) + \frac{1}{2}\tilde{R} = \frac{1}{2\pi} \int_0^\infty \sigma(k'^2) dk'. \quad (8'')$$

We note (Byron *et al* 1975) that since for the rare gases $A > 0$ and $f_B^D > 0$ we must have $f_B^E > (A + f_B^D)$ to avoid contradiction since $\sigma(k^2)$ is necessarily non-negative.

3. Electron scattering by atomic hydrogen

Trivially,

$$f_B^D(0, 0) = 1.0 \quad f_B^E(0, 0) = 6.0$$

while (Schwartz 1961) the scattering lengths are $a^+ = 5.965$, $a^- = 1.768$ giving

$\tilde{A} = 2.82$. Thus the sum rule (8'') becomes

$$\frac{1}{2}\tilde{R} = 0.82 + \frac{1}{2\pi} \int_0^\infty \sigma(k^2) dk. \quad (11)$$

Consider the total cross section. Below the inelastic threshold ($k^2 = 0.75$) we adopt the elastic cross sections calculated using the variational phaseshifts of Schwartz (1961), Armstead (1968) and Gailitis (1965). From threshold to 200 eV we adopt the hybrid (pseudostate close-coupling distorted-wave) 2s and 2p calculated cross sections of Callaway *et al* (1975) and McDowell *et al* (1975). These are within $\pm 10\%$ of the experimental values (normalized to Williams and Willis' (1974) value for σ_{2p} at 11.02 eV) of Long *et al* (1968) and Kauppila *et al* (1970). For $n = 3$ we adopt the values of Syms *et al* (1975), which are in close agreement with the experimental values of Mahan (1974). The ionization cross section is taken to be that of Boyd and Boksenberg (1959). The Born approximation is used in its Bethe-Born sum-rule form (Inokuti 1971, Inokuti and McDowell 1974) above 200 eV. The greatest uncertainty is attached to the adopted values of the total elastic cross section from 30 to 200 eV.

The contributions to the integral over the total cross section from various energy ranges are given in table 1. It is clear that errors of $\pm 20\%$ in the inelastic region, even if they were to add coherently, cannot leave an uncertainty of more than $\pm 10\%$ in the final result of $5.55 a_0$ for the weighted integral. With this value we require

$$\tilde{R}(0) = 12.74 \pm 1.11 \quad (12)$$

if the sum rule is to be satisfied.

The first attempt at evaluating \tilde{R} was made by Spruch and Rosenberg (1960). It is given by

$$\tilde{R}(0) = \frac{1}{2\pi|\epsilon(H^-)|} \left| \iint e^{-\alpha z_1} U_{1s}(r_2) \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) \omega(r_1, r_2) dr_1 dr_2 \right|^2 \quad (13)$$

where

$$\alpha = (\epsilon(H^-))^{1/2} \quad U_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r}$$

and $\omega(r_1, r_2)$ is the H^- ground-state wavefunction. Spruch and Rosenberg used the result of Ohmura and Ohmura (1960) that writing

$$\omega(r_1, r_2)|_{r_1=0, r_2=r} = C(r) e^{-\alpha r}/r \quad (14)$$

Table 1. Contributions to $I = (1/2\pi) \int_0^\infty \sigma(k^2) dk$ for (e^-, H) ($k_1 \leq k \leq k_2$).

k_1	k_2	ΔI
0.0	0.2	1.32
0.2	0.5	1.05
0.5	0.8	0.54
0.8	1.49	0.56
1.49	3.84	0.90
3.84	∞	1.18
Total		5.55

then $C(r)$ tends to a constant as $r \rightarrow \infty$. They found that using the 202-parameter Pekeris function (Pekeris 1958), $C(\infty) = 0.125874$. With this result (13) is readily evaluated to give $11.3 a_0$.

We were unable to obtain details of the Pekeris wavefunction, but used a number of other accurate functions due to Williamson (1942), Henrich (1944), Hart and Herzberg (1957), and 22-, 34- and 70-parameter functions due to C Schwartz (private communication to Dr A E Kingston). The Schwartz functions are of the form

$$\omega(r_1, r_2) = \exp[-\epsilon(r_1 + r_2)] \sum_{l, m \geq n} a_{lm} r_1^l r_2^m (r_1^m r_2^n + r_2^m r_1^n) \quad (l, m, n \geq 0)$$

and with 70 terms give an H^- binding energy of 0.0277475 au ($\alpha = 0.2356$) in agreement with Pekeris' result to four significant figures. The analysis is straightforward, though lengthy, and our results are given in table 2. We have also used the Spruch-Rosenberg approach on a number of these functions. The anomalous result obtained with the 50-term Schwartz wavefunction (which yields a residue of $10.4 a_0$) indicates that the convergence of the values of $\bar{R}(0)$ is not uniform as the number of terms in the wavefunction is increased, and that convergence of $\bar{R}(0)$ to a value 11.3 (obtained with the 70-term Schwartz wavefunction) cannot be considered established. However use of the Spruch-Rosenberg asymptotic evaluation (with their choice of values of r_1 and r_2 , i.e. $r_1 = 0$ and $r_2 = 15 a_0$) gives a sequence of values of $\bar{R}(0)$ which appear to tend to the value of $11.3 a_0$ they obtained with the Pekeris wavefunction.

The values obtained suggest, but do not prove, that the value of $11.3 a_0$ obtained by Spruch and Rosenberg is accurate, and it is difficult to see how any further improvement in the wavefunction could yield a value ($12.74 \pm 1.11 a_0$) consistent with the sum rule. Thus on the available evidence the zero-energy sum rule fails for electron-hydrogen scattering.

The subtracted dispersion relation

$$\begin{aligned} \text{Re } f(0, k^2) + \tilde{A} \\ &= \frac{1}{2}(f_B^E(0, 0) - f_B^E(0, k^2)) + \frac{k^2 P}{4\pi} \int_0^\infty \frac{\sigma(k'^2) dk'^2}{(k'^2 - k^2)k'} + \frac{1}{2}(\tilde{R}(0) - \tilde{R}(k^2)) \\ &= \frac{1}{2}(f_B^E(0, 0) - f_B^E(0, k^2)) + \frac{k^2 P}{4\pi} \int_0^\infty \frac{\sigma(k'^2) dk'^2}{(k'^2 - k^2)k'} \\ &\quad + \frac{\tilde{R}(0)}{2\epsilon} \left[1 - \left(1 + \frac{k^2}{\epsilon} \right)^{-1} \right] \end{aligned} \quad (8')$$

Table 2. Evaluations of $\bar{R}(0)$, the H^- residue, in a_0 .

Wavefunction	No of terms	Exact	Asymptotic†
Williamson	6	11.8	—
Henrich	11	11.5	—
Hart and Herzberg	20	9.6	10.4
Schwartz	22	11.4	5.4
	34	11.4	5.8
	50	10.4	8.5
	70	11.3	11.1
Pekeris	203	—	11.3

† The asymptotic form evaluated with $r_1 = 0$, $r_2 = 15 a_0$.

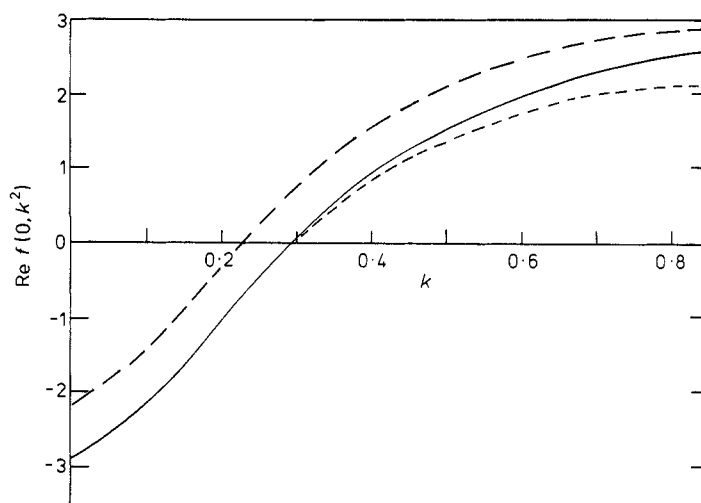


Figure 1. $\text{Re } f(0, k^2)$ for low-energy electrons in atomic hydrogen. The upper broken curve is the unsubtracted result (8), the lower broken curve the subtracted result (8') and the full curve the left-hand side of (8) evaluated using accurate phaseshifts (see text).

should, and does, hold for $k^2 \ll 1.0$ if our adopted cross sections are correct. The subtracted and unsubtracted versions are compared in figure 1 with the values of $\text{Re } f(0, k^2)$ obtained using the accurate variational phaseshifts for $l = 0, 1, 2$, together with Born values for a polarization potential for $l \geq 3$. This suggests that although it may be invalid, the dispersion relation, particularly after subtraction, may nonetheless be a useful guide.

4. Electron scattering by helium

We again consider the zero-energy sum rule, equation (3'') above. The Born direct amplitude is accurately known (Pekeris 1959): $f_B^D(0,0) = 0.791$. The scattering length is best determined from the very low-energy diffusion cross section measurements (Crompton *et al* 1967, 1970), and their value of $(1.18 \pm 0.01) a_0$ agrees well with those obtained from *a priori* theoretical calculations and from a phaseshift analysis of low-energy scattering (Naccache and McDowell 1974). The total cross section $\sigma(k^2)$ and the Born exchange amplitude remain to be determined.

We first consider the values to be adopted for the total cross section. In the elastic region direct absorption measurements at energies up to 22 eV were made by Golden and Bandel (1965). Somewhat higher values were obtained by Andrick and Bitsch (1975) from an extrapolation to small angle and a phaseshift analysis of their differential cross section measurements. These results, together with both the similar results of McConkey and Preston (1975), Sethuraman *et al* (1974), Crooks (1972) and other workers and values obtained from the theoretical phaseshifts of LaBahn and Callaway (1970) and Sinfailam and Nesbet (1972) have been carefully analysed by de Heer and Jansen (1975a). Their adopted values agree above 7 eV with those obtained from our phaseshift analysis. We used the same data as Naccache and McDowell (1974) except for the total cross section above 20 eV, where we took

Table 3. Total cross sections for electron scattering by helium (πa_0^2).

$E(\text{eV})$	1	2	3	4	5	6	7	8
Q	6.50	6.65	6.58	6.42	6.22	6.01	5.80	5.53
E	9	10	11	12	13	14	15	16
Q	5.29	5.09	4.95	4.69	4.49	4.31	4.15	4.00
E	17	18	19	20	30	40	50	60
Q	3.87	3.75	3.65	3.57	2.73	2.32	2.03	1.82
E	70	80	90	100	150	200	300	400
Q	1.65	1.51	1.40	1.30	1.03	0.85	0.65	0.50

the values recommended by de Heer and Jansen, while we also include the differential cross sections of Gupta and Rees (1975) at 100 eV. We find a better fit to the diffusion cross section data, which are probably more accurate below 7 eV than any of the other measurements, by supposing that the total elastic cross sections fall slowly from the Andrick and Bitsch curve at 7 eV to Golden and Bandel's value at 1 eV. Our adopted cross sections are given in table 3. At energies between 20 and 400 eV we take de Heer and Jansen's values and above 400 eV we use the Born total cross sections (Inokuti 1971, Inokuti and McDowell 1974, Kennedy 1968). The values above 100 eV are substantially larger than those obtained in the early measurements of Normand (1930), the correction factor at 400 eV being 1.67.

With these values the contributions to the sum-rule integral from various energy ranges are as shown in table 4. No particular energy range dominates. We estimate the overall uncertainty as $\pm 8\%$, assuming the Born approximation is correct to within 5% above 1000 eV, and that the low-energy diffusion measurements ($k < 0.81$) are at least as reliable. This allows for $\pm 10\%$ uncertainty from 7 eV to 1000 eV, which is probably generous. Thus taking the integral to be 2.564 ± 0.26 we would require the value of $f_{\text{B}}^{\text{E}}(0.0)$ to be 4.50 ± 0.30 for the sum rule to hold.

Table 4. Contributions to $I = (1/2\pi)\int_0^\infty \sigma dk$ from $k_1 \leq k \leq k_2$ for (e^- , He).

k_1	k_2	ΔI
0	0.5147	0.7052
0.5147	0.8088	0.1545
0.8088	1.4338	0.1987
1.4338	7.2426	0.5058
7.2426	75.00	0.5477
75.00	∞	0.4518
Total		2.564

The Born exchange amplitude reduces to the simple form

$$g^{(\text{L})} = f_{\text{B}}^{\text{E}}(0, 0) = -\frac{1}{2\pi} \int \phi^*(2, 3) \left(\frac{1}{r_{13}} + \frac{1}{r_{23}} - \frac{2}{r_3} \right) \phi(1, 2) d\tau_{123}$$

at zero energy, $\phi(i, j)$ being the ground-state wavefunction of helium with electrons i and j bound. Provided ϕ is the exact ground state, an equivalent form is (McDowell 1974)

$$g^{(\text{V})} = -\frac{1}{2\pi} \int \phi^*(2, 3) \left(\frac{1}{r_{13}} + \frac{2}{r_2} + E_0 + \frac{1}{2} \nabla_2^2 \right) \phi(1, 2) d\tau_{123}.$$

We have evaluated these expressions with the following choices of approximate $\phi(1, 2)$.

(i) One-parameter variational:

$$\phi_1(1, 2) = N_1 \exp[-\alpha(r_1 + r_2)] \quad \alpha = 1.6875.$$

(ii) Two-parameter open-shell (Eckart 1930):

$$\phi_2(1, 2) = N_2(\exp(-\alpha r_1 - \beta r_2) + \exp(-\alpha r_2 - \beta r_1)).$$

(iii) Analytic Hartree-Fock:

$$\phi_3(1, 2) = \psi(1)\psi(2) \quad \psi(i) = N_3(\exp(-\alpha r_i) + c \exp(-\beta r_i))$$

with $\beta = 2$, $\alpha = 1.4558$ (Green *et al* 1954).

(iv) $\alpha = 1.41$, $\beta = 2.61$ (Byron and Joachain 1966).

(v) Two-parameter Hylleraas (Baber 1937):

$$\phi_5(1, 2) = N_4 \exp[-\alpha(r_1 + r_2)] (1 + cr_{12})$$

with $\alpha = 1.849$, $c = 0.364$.

(vi) Three-parameter Hylleraas (Green *et al* 1953):

$$\phi_6(1, 2) = N_6 \exp[-\alpha(r_1 + r_2)] [1 + A(r_1 - r_2)^2 + Br_{12}]$$

with $\alpha = 1.816$, $A = 0.13$, $B = 0.3$.

(vii) Six-parameter Hylleraas (Lawson *et al* 1966):

$$\begin{aligned} \phi_7(1, 2) = N_7 \exp[-\alpha(r_1 + r_2)] \\ \times [1 + A(r_1 + r_2) + B(r_1^2 + r_2^2) + Cr_1r_2 + Dr_1r_2 \cos \theta_{12} + Er_{12}] \end{aligned}$$

with $\alpha = 1.82$, $A = 0.10083$, $B = 0.12985$, $C = 0.19079$, $D = 0.063598$, $E = 0.3538$.

Wavefunctions (viii)–(xi) are configuration interaction wavefunctions obtained using the program CIV3 due to Hibbert (1975) with the following 1S_0 configurations:

(viii) $(1s)^2, (2s)^2, (2p)^2$;

(ix) $(1s)^2, (2p)^2, (3p)^2, (3d)^2$;

(x) $(1s)^2, (2s)^2, (2p)^2, (3s)^2, (3p)^2$;

(xi) $(1s)^2, (2s)^2, (2p)^2, (3s)^2, (3p)^2, (3d)^2$.

A full account of the analysis is given elsewhere (Rabheru 1975). The results are

Table 5. The zero-energy Born amplitude for helium.

Wavefunction	$g^{(L)}$	$g^{(V)}$
(i)	3.147	2.458
(ii)	4.230	4.621
(iii)	3.832	3.788
(iv)	3.900	3.931
(v)	3.319	2.698
(vi)	3.795	3.176
(vii)	3.831	3.292
(viii)	3.902	3.874
(ix)	3.902	4.672
(x)	3.901	3.895
(xi)	3.920	3.911

presented in table 5. The Hylleraas functions give poor $g^{(V)}$ values. Our $g^{(L)}$ value for the six-parameter Hylleraas function is 3.831 close to the value of 3.833 obtained with the simple Hartree-Fock function. Lawson *et al* (1966), who used both these functions, apparently obtained a significantly higher result of about 4.2 using the Hylleraas function, though they do not quote their result directly. Evaluation of $g^{(L)}$ using this function requires evaluation of an integral of the form

$$\int \frac{r_{12}r_{23}}{r_{13}} \exp(-\alpha r_1 - \beta r_2 - \gamma r_3) d\tau_{123}.$$

Our result for this integral agreed with that obtained by Moussa and Radi (1973) to four figures.

The values quoted in table 5 suggest that a converged value of $f_B^E(0,0)$ for helium will be 3.92 ± 0.05 and this is the value we adopted.

It follows that the sum rule does not hold, though *the result is not conclusive*, as we have no bound on the error associated with our best value of $g_B(0,0)$.

5. Elastic scattering of electrons by lithium

We have attempted to extend our analysis to electron scattering by lithium. However few of the relevant quantities are accurately known.

Variational (Sinfailam and Nesbet 1973) and close-coupling calculations (two-state, Burke and Taylor 1969; three-state, Norcross 1971) give consistent values of the singlet and triplet scattering lengths, and we may take $\tilde{A} = -4.58$. The direct part of the zero-energy Born amplitude may be obtained from the form factor using analytic Hartree-Fock wavefunctions (Inokuti and McDowell 1974) as

$$f_B^D(0, k^2) = 6.211$$

and is unlikely to be in error by more than 5%.

We have evaluated $g_B(0,0)$ using ground-state wavefunctions due to Walters (1973), Clementi (1965) and the unrestricted Hartree-Fock function of Sachs (1960). Details of the analysis are given elsewhere (Rabheru 1975) and the results are presented in table 6. The adopted value is $g_B(0,0) = 70.0 a_0$, but the uncertainty may be as large as 10% as configuration interaction effects may be significant.

Total cross sections for electron scattering by lithium have been measured by Kasdan *et al* (1971 and private communication) at energies up to 50 eV. Below 20 eV they are in fair agreement with the close-coupling calculations, and at low energies (≤ 5 eV) with the variational results of Sinfailam and Nesbet (1973). The situation

Table 6. Zero-energy Born exchange amplitude for electron-lithium scattering.

Wavefunction	$g^{(L)}$	$g^{(V)}$
Walters (1973)	71.556	91.206
RHF†	69.375	69.354
UHF‡	69.528	69.664

† RHF, restricted Hartree-Fock.

‡ UHF, unrestricted Hartree-Fock.

at energies above 20 eV, where there appears to be a discrepancy. has recently been reviewed by Walters (1976) who suggests a downward renormalization of the experimental values in this energy range by about 25%. For our purposes this is unimportant, as the sum-rule integral is dominated by the very large elastic cross section at energies below 5 eV. Any reasonable extrapolation to the Born values (Inokuti and McDowell 1974) at high energies yields

$$\frac{1}{2\pi} \int_0^\infty \sigma(k^2) dk = 80 \pm 8.$$

It follows that if the zero-energy sum rule is to hold, the residue of the Li^- bound state must lie in the range $84 \leq \tilde{R} \leq 104$.

The available Li^- ground-state wavefunctions, of which the most elaborate appears to be a 14 configuration CI wavefunction due to Weiss (1968 and private communication from Dr D L Moores) which includes orbitals up to 4f, yield much too large a value for \tilde{R} . This may be due to their inability to adequately describe the asymptotic region. We suggest that alternatives to variational methods based on energy minimization must be sought if a Li^- ground-state wavefunction sufficiently accurate to test the sum rule is to be obtained.

6. Elastic scattering of electrons by neon

We again attempt a test of the zero-energy sum rule, equation (3'') above. Naccache and McDowell (1974) obtained a scattering length of $(0.22 \pm 0.005)a_0$ from their phaseshift analysis; this value relied heavily on the low-energy diffusion cross section measurements of Robertson (1972). However it is in good accord with that obtained from quantal calculations (Thompson 1971, Blum and Burke 1975). Peixoto *et al* (1969) have given configuration interaction calculations of the form factor $F(K)$, from which we derive a forward Born direct amplitude $f_B^D(0, k^2) = 3.210$, while Knowles (1973) has evaluated $g_B^{(L)} = f_B^E(0, 0)$ using Hartree-Fock wavefunctions and finds $f_B^E(0, 0) = 5.321 \pm 0.2$. Thus the sum rule will be satisfied provided

$$\frac{1}{2\pi} \int_0^\infty \sigma(k^2) dk < 1.90 \pm 0.20.$$

Naccache and McDowell (1974) evaluated the integral by taking Salop and Nakano's (1970) measurements of the total cross section up to 20 eV, and the Bethe-Born values (Dehmer and Saxon 1973, 1975 (see also Inokuti *et al* 1975), Inokuti and McDowell 1974) above 400 eV, interpolating in the intermediate energy range. They found $(1/2\pi) \int_0^\infty \sigma dk \geq 4.5$, and judged that the sum rule failed. However, de Heer and his colleagues (Jansen *et al* 1974) and Bromberg (1974) have shown that the Born approximation is invalid at 400 eV for elastic scattering of electrons by neon, and in fact grossly overestimates there. We therefore adopted the values of the total cross section given by Jansen *et al* from 100 eV to 3 keV, using the Bethe-Born values only at energies in excess of this. There are no small-angle absolute differential elastic or inelastic measurements, nor any recent total cross section measurements below 100 eV (Williams and Crowe 1975). The data of Normand (1930) is suspect, and theoretical methods currently available are unreliable above 20 eV and below,

Table 7. (a) Adopted total cross sections for electron scattering by neon (πa_0^2).

$E(\text{eV})$	10	20			
σ	3.79	4.10	(Salop and Nakano 1970)		
$E(\text{eV})$	40	60	80		
σ	4.01	3.87	3.22	(interpolated)	
$E(\text{eV})$	100	300	500	1000	300
σ	3.22	2.05	1.52	0.98	0.41 (de Heer and Jansen 1975)

Table 7. (b) Contributions to the weighted sum rule integral from ranges $k_1 \leq k \leq k_2$.

k_1	k_2	ΔI
0	1.22	0.533
1.22	2.71	0.875
2.71	4.70	0.840
4.70	∞	2.879

$$(1/2\pi) \int_0^\infty \sigma dk = 5.13 \pm 0.60 a_0.$$

say, 200 eV. Thus we are forced to follow Naccache and McDowell's procedure for this energy range. Our adopted values, and the contributions to the integral from various energy ranges are given in table 7. To obtain the asymptotic contribution we followed Bransden and Hutt (1975) in fitting an expression of the form

$$\sigma(k^2) = \frac{1}{k^2} \left(63.3 + 7.7 \ln k^2 + \frac{A}{k^2} + \frac{B}{k^4} \right) (\pi a_0^2) \quad k^2 > 20.0$$

where the first two coefficients give the leading Born terms (Inokuti and McDowell 1974) to the data of Jansen *et al* (1976) and de Heer and Jansen (1975) at 300 and 1000 eV. We find $A = -2480$ and $B = 50020$.

In this case the integral is dominated by the large cross sections at impact energies above 300 eV. The values given by de Heer and Jansen (1975) are 21% larger than those of Normand (1930) at 400 eV. They are 13% higher at 1 keV than the measured values of Jansen *et al* (1976), and appear to be accurate to $\pm 20\%$. Our derived value of the sum-rule integral, which relies directly on the values given by de Heer and Jansen, is 5.13 ± 0.60 , consistent with the earlier estimate by Naccache and McDowell (1974). The values of the total cross section measured by Jansen *et al* (1976) at 3 keV is $0.57 \pi a_0^2$, substantially higher than the value recommended by de Heer and Jansen (1975) which we adopted. Thus our value for the integral is unlikely to be an overestimate.

Unless the Hartree-Fock value of $f_B^E(0,0)$ or the total cross sections adopted, or both, are grossly in error, we must conclude that the sum rule fails in this case also. It is of interest to note that in the three cases (H, He, Ne) where we can reach a conclusion, we find that the discrepancy has the same sign, i.e. the value of the sum-rule integral obtained from the measured cross sections is too large.

7. Conclusions

We have shown that an analysis of current experimental data, together with a careful evaluation of the Born amplitudes for elastic scattering and, in the case of atomic

hydrogen, the $H^{-}(^1S_0)$ residue, suggests clearly that the zero-energy form of the Gerjuoy-Krall dispersion relation does not hold for electron scattering. No conclusion was possible for lithium.

Bransden and Hutt (1975), on the other hand, found, using the data of Coleman *et al* (1976) that this relation held for scattering of positrons by helium, and, with less certainty, by neon. The measurements of Dutton *et al* (1975) reinforce this conclusion. The only difference in the two cases is that the elastic amplitude has no exchange term for positron scattering. We have seen already (§2) that in the electron case the sum rule cannot be made to hold merely by dropping the exchange term. The implication is that there are singularities present in the exchange amplitudes, which do not cancel those in its Born term.

It is readily seen (R Shakeshaft 1975, private communication) in the case of atomic hydrogen that $f_B^E(\theta, k^2)$ contains an additional singularity. We have

$$f_B^E(\theta, k^2) = \frac{1}{2\pi} \int \phi_{1s}(r_1) \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) \phi_{1s}(r_2) \exp(i\mathbf{k}_i \cdot \mathbf{r}_1 - i\mathbf{k}_f \cdot \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

with $|\mathbf{k}_i| = |\mathbf{k}_f| = k$. Thus

$$\begin{aligned} f_B^E(\theta, k^2) &= \frac{1}{2\pi^2} \int \exp[-(r_1 + r_2)] \exp[i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2\pi} \int \exp[-(r_1 + r_2)] \exp[i(\alpha + i\beta)|\mathbf{r}_1 - \mathbf{r}_2| \cos \theta] V(r_1, r_2) d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned}$$

where we have written $k = \alpha + i\beta$, so that provided $\beta > -1$ there exist some θ , namely $\theta = \cos^{-1}(\hat{\mathbf{k}}_1 \cdot \hat{\mathbf{R}}) = 0$ for which the integral diverges as $|\mathbf{R}| = |\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty$. This singularity occurs at minus the binding energy of the target electron in the k^2 plane. The same is true for any other atom in which the exchange electron while bound is in an orbital behaving asymptotically as $\exp(-E_b^{1/2}r)$.

In the case of atomic hydrogen we can evaluate the above integral exactly (Byron *et al* 1975), and the singularity turns out to be a pole of order three at $k^2 = 1.0$ with a non-vanishing contribution to the contour integral. Thus if $Q(\theta, k^2)$ is to have the desired analytic structure, the residue of this third-order pole must be exactly cancelled by the corresponding contributions from the exact exchange amplitude.

Blum and Burke (1975) have considered a model problem, specifically electron-hydrogen scattering in the static-exchange approximation. Again the first Born exchange term has a third pole at $k^2 = 1$, as does the second-order term. It follows that in this case $Q(\theta, k^2)$ cannot have the required analytic structure, independent of the nature of the singularity in the higher Born terms, unless the sum of these in third and higher orders exactly cancels the second Born contribution at $k^2 = -1$. Blum and Burke have shown that numerical checks of the dispersion relation ($k^2 > 0$) and the sum rule both fail in their model problem when exchange is included.

Further work is required to establish the correct singularity structure of the full exchange amplitude in a real problem. An interesting, but not quite convincing, discussion for $e^{-}\text{-He}$ is given by Peccei and Viollier (1976). They suggest that the Born exchange term should be replaced by poles arising from the ground and all excited states of $(\text{He}^+ + e)$, together with the left-hand cut from its continuum. The leading such pole is $(\text{He}^+(1s\ ^2S_0) + e)$ which is the third-order pole occurring in $f_B^E(0, k^2)$, and they argue that use of $g_B(0, k^2)$ approximates the left-hand terms by

this leading pole. The difficulty is that these poles correspond to states of He and not of (He + e).

The existence of a left-hand cut analyticity in the region of $f(0, k^2)$, corresponding in the present case to exchange of the incident electron with an initially bound electron, has been established in the case of general three-body scattering with rearrangement by Rubin *et al* (1967). Their analysis was restricted to short-range interactions, so that their detailed conclusions cannot be taken over directly in the electron-atom case, where the interactions are Coulombic. Nevertheless the additional complications introduced by the Coulomb interaction are not expected to significantly change the analytic structure of the amplitudes. The mere existence of a left-hand cut does not in itself indicate that the Gerjuoy-Krall dispersion relation is false; the question to be answered is whether the cut in $f(\theta, k^2)$ is cancelled exactly by that in $f_B(\theta, k^2)$ or not.

Acknowledgments

This work was carried out under an SRC Research Grant B/RG/2606-7. We are indebted to Professor B H Bransden, Dr F J de Heer, Professor P G Burke and other colleagues for helpful discussions.

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