

## Angular Dependence of $2^3S$ Excitation of He by High-Energy Electron Impact

IK-JU KANG AND CHAN KYOO CHOI

*Department of Physics, Southern Illinois University, Carbondale, Illinois*

(Received 21 February 1968)

Electron impact excitation of metastable He atoms is formulated in the Coulomb-wave approximation. At high energy, both the direct and the exchange scattering amplitudes are approximated in closed analytic forms, which are identical to the Born-Oppenheimer approximation apart from the core potential contribution. From these expressions, the validity of the Ochkur approximation and its limitations are discussed. Also obtained is the forward-peaking differential cross section for He( $2^3S$ ) excitation, which is in qualitative agreement with the recent experiment by Vriens, Simpson, and Mielczarek. Thus an explanation for the observed angular behavior of the cross section is offered for the first time.

### INTRODUCTION

RECENTLY the differential cross sections for high-energy electron impact excitation of the metastable states of helium atoms have been reported by Vriens, Simpson, and Mielczarek.<sup>1</sup> They observed that the  $2^3S$  excitation cross section peaks in the forward direction, a fact which cannot be explained by the Ochkur approximation<sup>2</sup> within the Born-Oppenheimer formulation. Most previous theoretical calculations<sup>3</sup> have been concerned with the total cross sections for these processes, so that there is no calculation with which the experimental results can be compared.

This paper reports a theoretical prediction of such a forward-peaking angular dependence of the cross section. Thus, the validity of the Born-Oppenheimer approximation for the description of the triplet excitation at high energy, which has not as yet been determined,<sup>4</sup> is demonstrated for this example. At the same time, it is shown what has gone wrong with the Ochkur approximation in failing to predict the observed behavior.

### FORMULATION AND CALCULATION

Following the recent work by Kang,<sup>5</sup> the differential cross sections for excitation of  $2^1S$  and  $2^3S$  states of helium atoms by unpolarized electron impact are given by<sup>6</sup>

$$\frac{d\sigma(2^1S)}{d\Omega(2^3S)} = \frac{k}{k_0} \left( \frac{|\sqrt{2}f - g/\sqrt{2}|^2}{3|g/\sqrt{2}|^2} \right), \quad (1)$$

<sup>1</sup> L. Vriens, J. A. Simpson, and S. R. Mielczarek, Phys. Rev. **165**, 7 (1968).

<sup>2</sup> V. I. Ochkur, Zh. Eksperim. i Teor. Fiz. **45**, 734 (1963) [English transl.: Soviet Phys.—JETP **18**, 503 (1964)]; V. I. Ochkur and V. F. Brattsev, Opt. i Spektroskopiya **19**, 490 (1965) [English transl.: Opt. Spectry. (USSR) **19**, 274 (1965)].

<sup>3</sup> H. S. W. Massey and B. L. Moisewitsch, Proc. Roy. Soc. (London) **A227**, 38 (1954); K. L. Bell, H. Eissa, and B. L. Moisewitsch, Proc. Phys. Soc. (London) **88**, 57 (1966), and references therein.

<sup>4</sup> See, for example, Charles J. Joachain and Marvin H. Mittleman, Phys. Rev. **140**, A432 (1965); **151**, 7 (1966).

<sup>5</sup> I. J. Kang, Phys. Letters **26A**, 25 (1967).

<sup>6</sup> If one writes  $(d\sigma/d\Omega)(2^1S) = (k/k_0)|f_1 - g_1|^2$  and  $(d\sigma/d\Omega)(2^3S) = 3(k/k_0)|g_3|^2$ , then  $f_1 = \sqrt{2}f$  and  $g_1 = g_3 = g/\sqrt{2}$ . Then the Ochkur

where  $\mathbf{k}_0$  and  $\mathbf{k}$  denote the momenta of the incoming and outgoing electrons, and  $f$  and  $g$  are the direct and exchange scattering amplitudes, defined as follows:

$$f = \frac{1}{2\pi} \left\langle \chi_1^{(-)}(\mathbf{k})\eta_2(2s) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_1^{(+)}(\mathbf{k}_0)\eta_2(1s) \right\rangle \quad (2)$$

and

$$g = \frac{1}{2\pi} \left\langle \chi_2^{(-)}(k)\eta_1(2s) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_1^{(+)}(\mathbf{k}_0)\eta_2(1s) \right\rangle. \quad (3)$$

In the above,  $\chi_1^{(-)}(\mathbf{k})$  and  $\eta_2(1s)$  denote the outgoing continuum state with momentum  $\mathbf{k}$  and the  $1s$  bound-state hydrogenic wave functions of  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , respectively. Atomic units are used throughout.

As an approximation, we take  $\chi^{(\pm)}(\mathbf{k})$  to be a plane wave (which can be justified at high energy) and the effective atomic number to be  $Z=27/16$ . Then the  $f$  and the  $g$  become identical to those of the Born-Oppenheimer approximation for electron scattering by hydrogenlike atoms with  $Z=27/16$ , except for the

TABLE I. The direct and the exchange amplitudes and the branching ratio of the triplet to the singlet metastable states of He in electron impact excitation. Here  $Z=27/16$ ;  $k_0^2=16.5$ .

Scattering angle	$f$ (direct)	$g$ (exchange)	$2^3S(\Omega)/2^1S(\Omega)$	
			Present theory	Vriens <i>et al.</i> <sup>a</sup>
0°	$33.4 \times 10^{-2}$	$14.1 \times 10^{-2}$	$21.4 \times 10^{-2}$	
1°	33.3	12.6	16.2	
2°	33.1	9.28	7.98	
3°	32.8	6.24	3.33	
4°	32.3	4.19	1.44	
5°	31.7	2.98	0.73	$0.44 \times 10^{-2}$
10°	27.1	1.82	0.361	0.54
15°	21.4	2.23	0.913	0.78
20°	15.8	2.60	2.42	
25°	11.2	2.74	5.89	
30°	7.70	2.68	13.3	

<sup>a</sup> Reference 1.

relation  $g = (q^2/U)f$  may be written as  $g_1 = f_1 q^2/(2U)$ , as noted by Vriens *et al.* (Ref. 1). It should be emphasized that  $g_1 = g_3/\sqrt{2}$  is found not to be satisfied. It may be added that the expressions in Eq. (1) yield  $(d\sigma/d\Omega)(2^1S) + (d\sigma/d\Omega)(2^3S) = 2(k/k_0)(f^2 + g^2 - fg) = 2(d\sigma/d\Omega)[H(1s) \rightarrow H(2s)]$ , as expected.

core-potential contribution to the  $g$  amplitude. Following the method of Corinaldesi and Trainor<sup>7,8</sup> without making any approximations, we find, after some tedious calculations, that

$$\sqrt{2}f/Z^4 = 16/D^3 \quad (4)$$

and

$$\begin{aligned} \sqrt{2}g/Z^4 &= \left( \frac{2}{Z} + \frac{\partial}{\partial \alpha_2} \right) \frac{\partial^2}{\partial \alpha_1 \partial \alpha_2} \frac{2}{b} \tan^{-1} \frac{b}{\beta} \Big|_{\alpha_n = z/n} \\ &= \frac{1}{UD^3} \left[ 16q^2 - \frac{4Z^2D}{U} + \frac{28Z^2D^2}{U^2} - \frac{60Z^4D}{U^2} - \frac{36Z^6}{U^2} + \frac{8Z^6D}{U^3} - \frac{8Z^4D^2}{U^3} \right] + \frac{1}{U^3q^2} \left[ -\frac{9Z^6}{D^2} + \frac{18Z^6}{UD} - \frac{18Z^8}{UD^2} - \frac{3Z^4}{U} \right] \\ &\quad + \frac{8Z^2}{U^3D^2q^2} \left[ (\mathbf{k}_0 \cdot \mathbf{q})(\mathbf{k} \cdot \mathbf{q}) \left( 5 - \frac{4Z^2}{U} + \frac{4q^2}{D} \right) - k_0^2 k^2 \sin^2 \theta \right] + \frac{4Z}{U^3q^4} \left( \frac{1}{q} \tan^{-1} \frac{2q}{3Z} - \frac{3Z}{2D} \right) \\ &\quad \times \left[ -8(\mathbf{k}_0 \cdot \mathbf{q})(\mathbf{k} \cdot \mathbf{q}) + k_0^2 k^2 \sin^2 \theta \left( 4 + \frac{9Z^4 - 3Z^2D}{2Uq^2} \right) - \frac{3Z^2}{U} \{ k^2(\mathbf{k}_0 \cdot \mathbf{q}) + (\mathbf{k} \cdot \mathbf{q})(\mathbf{k}_0 \cdot \mathbf{k}) \} \right], \quad (5) \end{aligned}$$

with

$$\begin{aligned} q^2 &= (\mathbf{k} - \mathbf{k}_0)^2 = k_0^2 + k^2 - 2k_0k \cos \theta, \\ U &= k_0^2 + \frac{1}{4}Z^2, \quad D = q^2 + 9Z^2/4, \\ \beta &= \alpha_1(k_0^2 + \alpha_2^2) + \alpha_2(k^2 + \alpha_1^2), \\ \mathbf{b} &= (k_0^2 + \alpha_2^2)\mathbf{k} - (k^2 + \alpha_1^2)\mathbf{k}_0. \end{aligned} \quad (6)$$

### DISCUSSION

In the high-energy region, one obtains the Ochkur relation

$$g \cong f(q^2/U) \quad (7)$$

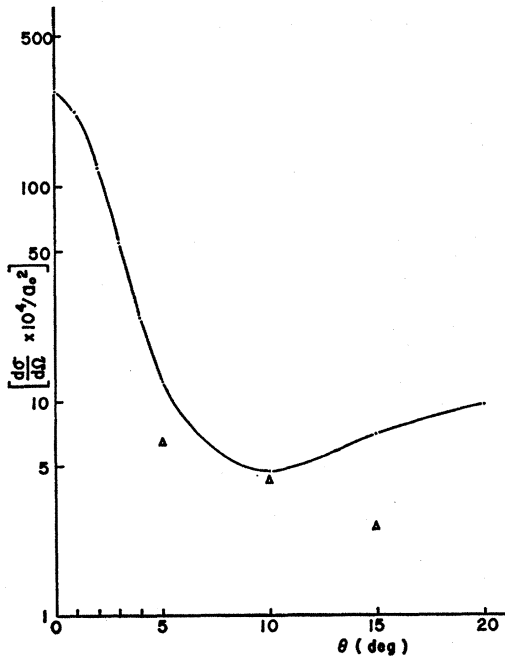


FIG. 1. The differential cross sections for the excitation of the  $2^3S$  state of He atoms by 225-eV electron impact. —, present theory;  $\Delta$  Vriens *et al.* (Ref. 1).

<sup>7</sup> E. Corinaldesi and L. Trainor, *Nuovo Cimento* **9**, 940 (1952). Their expression for  $Z^2g'\{1/r_{12}\}$  does not seem to agree with the  $g$  in Eq. (6).

<sup>8</sup> I. J. Kang, *Phys. Rev.* **144**, 29 (1966).

provided that the square of the momentum transfer is not too small, so that the first term is the dominant one in magnitude. However, this will not be the case when the scattering angle is so small that

$$q^2 \ll Z^2 \quad \text{and/or} \quad Uq \ll Z^3. \quad (8)$$

Therefore, the Ochkur approximation becomes inadequate for some small-angle scattering with  $Z \gg 1$ . Depending on the energy of the incoming electron and the effective atomic number, one can determine an angle above which the Ochkur approximation is valid and below which it is not. This critical angle lies between  $10^\circ$  and  $15^\circ$  for the case of  $k_0^2 = 16.5$  and  $Z_{\text{eff}} = 27/16$ . It is for the purpose of exhibiting the behavior of the  $g$  amplitude for high-energy small-angle scattering that the lengthy Eq. (5) is displayed.

Numerical calculations were carried out for the differential cross section of the process. The results are shown in Fig. 1. Also calculated was the branching ratio of the triplet to the singlet excitation, tabulated in Table I. Comparison of the results of the present calculation with measurements<sup>1</sup> shows qualitative agreement,<sup>9</sup> exhibiting the peaking of the cross section in the forward direction, and at the same time, the increase of the branching ratio as the scattering angle increases beyond  $10^\circ$ .

It should be added that from the results of Corinaldesi and Trainor,<sup>7</sup> the high-energy behavior of the  $f$  and  $g$  amplitudes was extracted by Borowitz and Klein<sup>10</sup> in 1956. They found that  $f_{\theta=0} \sim Z^{-2}(1/n + 1/n_0)^{-6}$  (where  $n_0$  and  $n$  are the initial and the final principal quantum numbers), which is evident from Eq. (4); and  $g_{\theta=0} \sim Z^{-2}(k_0/Z)^{-4}$ , which is the behavior of the first term of our  $g$  in Eq. (5), namely  $Z^{-2}(k_0/Z)^{-4}(1/n + 1/n_0)^{-4}$ .

<sup>9</sup> For  $Z_{\text{eff}} = 1.41$ ,  $(d\sigma/d\Omega)(2^3S)$  also exhibits a similar forward-peaking behavior with its magnitude reduced by almost a factor of 2.

<sup>10</sup> S. Borowitz and M. M. Klein, *Phys. Rev.* **103**, 612 (1956). It would be interesting to investigate their claim that Eqs. (2) and (4) yield the same high-energy behavior while Eqs. (3) and (5) yield different ones.

However, it is emphasized that the additional terms of  $g$  in Eq. (5) behave for  $\theta=0^\circ$  like

$$\frac{Z^6}{U^3 q^2 \theta=0} \cong \frac{4}{Z^2} \left(\frac{k_0}{Z}\right)^{-4} \left(\frac{1}{n_0} \frac{1}{n}\right)^{-2} \left(\frac{1}{n_0} \frac{1}{n}\right)^{-2}. \quad (9)$$

It is the behavior of  $Z^6/(U^3 q^2)$  which is responsible for the peaking of the differential cross sections in the near forward direction. In fact, such an asymptotic behavior was predicted for excitation processes in 1966 by one of us (I. J. K.).<sup>8</sup> It was then conjectured that the excitation exchange amplitude for processes with  $(n_0-n)/n_0 \ll 1$  might even be dominant over the direct scattering amplitude in the forward direction, a prediction which may be tested experimentally in the future.

Finally, it is desirable to have more experimental results for the process, inasmuch as the data on total cross sections vary somewhat among the authors.<sup>11</sup> It is also conceded that there is room for improvement toward better quantitative agreement between theory and experiment in regard to the magnitude and fine structure of the differential cross section.

#### ACKNOWLEDGMENTS

One of us (I. J. K.) wishes to thank Dr. M. Inokuti, Dr. Y. K. Kim, Dr. J. A. Simpson, Dr. J. W. Copper, and Dr. R. E. Watson for helpful discussions.

<sup>11</sup> See, for example, Table IV in Ref. 1.

## Perturbation Theory for Exchange Interactions between Atoms and Molecules. I

A. B. RITCHIE

Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia 22901

(Received 12 January 1968; revised manuscript received 20 February 1968)

A perturbation theory has been developed for interatomic or intermolecular forces with exchange. The method requires the use of label-free operators in a representation of nonorthogonal, antisymmetrized states. The introduction of this representation shows that the explicit construction of a complete orthogonalized set is unnecessary. The antisymmetry of the exact wave function is preserved to all orders, and hence exchange is treated exactly.

### INTRODUCTION

RECENTLY, a number of papers<sup>1-4</sup> have appeared on the perturbation theory of interatomic or intermolecular forces at distances close enough so that exchange effects become important. Treatment of exchange entails the antisymmetrization of the zeroth-order representation of simple-product states for the particles at infinite separation, and this process destroys the orthogonality of the set and  $H_0$  as a diagonal operator. Jansen<sup>1</sup> has given a brief history of the problem and has recast the Rayleigh-Schrödinger (RS) series to handle it. The main idea of his paper is the *orthogonalization* of the antisymmetrized set and the introduction of label-free operators  $H_0'$  and  $V'$ , such that  $H_0'$  remains diagonal in the old antisymmetrized, *nonorthogonal* set. The extra terms which arise in the RS series are the matrix elements of  $H_0'$ , which is *not* diagonal in the orthogonalized set. The main difficulty in this treatment is the labor required to obtain a complete orthogonalized set.

Murrell and Shaw<sup>2</sup> have briefly criticized several other papers and have formulated a Brillouin-Wigner-type expansion for the exchange problem. The main idea is the definition of a projection operator,

$$O = |a\rangle\langle a| / \langle a|a\rangle \quad (1)$$

( $| \rangle$  means antisymmetrized and  $| \rangle$  means a simple-product-type function), which, since any function is projected along  $|a\rangle$ , insures the antisymmetry of the exact wave function. Formally,<sup>5,6</sup>

$$\Psi = |a\rangle + \frac{(I-O)}{E-H} H|a\rangle, \quad (2)$$

where  $I$  is the identity. The argument<sup>2</sup> is that in the equation

$$(I-O)(E-H)TH|a\rangle = (I-O)H|a\rangle \quad (3)$$

$H|a\rangle$  is antisymmetric (since  $H$  is symmetric in the electrons).  $O$  projects out an antisymmetric function; therefore  $(E-H)TH|a\rangle$  is antisymmetric, and since  $(E-H)$  is symmetric,  $TH|a\rangle$  is antisymmetric. Hence (2) is also antisymmetric. This antisymmetry is lost

<sup>1</sup> Laurens Jansen, Phys. Rev. **162**, 63 (1967), and references therein.

<sup>2</sup> J. N. Murrell and G. Shaw, J. Chem. Phys. **46**, 1768 (1967), and references therein.

<sup>3</sup> J. I. Musher and A. T. Amos, Phys. Rev. **164**, 31 (1967).

<sup>4</sup> Ad van der Avoird, J. Chem. Phys. **47**, 3649 (1967).

<sup>5</sup> R. Yaris, J. Chem. Phys. **44**, 3894 (1966).

<sup>6</sup> P. O. Lowdin, J. Math. Phys. **6**, 1341 (1965)