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Elastic scattering of fast electrons by $H_2(^1\Sigma_g^+)$ and $N_2(X\,^1\Sigma_g^+)$

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The differential cross section (DCS) $d\sigma^{\mathrm{el}}/d\Omega$ for the elastic scattering of electrons by homonuclear diatomic molecules in the first Born approximation at scattering angles equal or near zero is derived here by an expansion method. This method gives $d\sigma^{\mathrm{el}}/d\Omega=\alpha+\beta K^2+\gamma K^4+\cdots$, where α,β,γ are constants, and K is the momentum transfer. For H_2, the value α with vibrational corrections is calculated with use of the most accurate wave function given by Kolos and Wolniewicz (KW) and the values for the constants β and γ are evaluated from the Davidson and Jones (DJ) wave function. The resulting DCS's at small scattering angles are given for comparison with experiment. The disagreement between theory and experiment for H_2 is found when the scattering angle is less than 15 mrad at 25 keV (i.e., $K=0.6$ a.u.). The disagreement is very similar to the ones reported in the studies of Compton scattering and $(e,2e)$ reaction spectroscopy. The disagreement between theory and experiment at scattering angles near zero for N_2 are also reported. New experimental data for H_2 and N_2 at very small scattering angles may be needed in order to establish the disagreements reported here. The DCS for N_2 at large scattering angles is also calculated using an accurate multiconfiguration self-consistent-field first-order configuration-interaction (MCSCF-FOCI) wave function. Good agreement within experimental resolution at large scattering angles is found for N_2 for the difference function $\Delta N(K)$ and for the DCS. This is contrary to the recent study of H_2 where discrepancies were reported at large scattering angles. The calculated total cross sections for N_2 are in good agreement with the experimental data at low incident energies is the hundred-electron-volt range.

I. INTRODUCTION

The investigation of the electronic charge density for atoms and molecules became an important topic in the late 1960's. Many tools have been developed subsequently for this purpose, for example, Compton profile studies, electron diffraction, electron impact spectroscopy, and very recently $(e,2e)$ reaction spectroscopy.[1] Since H_2 is the simplest molecule, the Compton profile and $(e,2e)$ reaction spectroscopy which are related to the Fourier transform of the molecular charge density have been studied in great detail.[2] For high-energy electron scattering, unfortunately, the differential cross sections (DCS's) of elastic scattering at scattering angles near zero are not thoroughly investigated. Instead the total difference function which has a direct relationship to the molecular binding energy has been studied in detail.[3] It is well understood that the DCS at small scattering angles is directly related to the electron charge distribution away from the nuclei. This is equivalent to the study of the Compton profile $J(q)$ at q near zero or the study of $(e,2e)$ reaction cross section which is directly related to the momentum density $\rho(p)$ at p near zero (see Refs. 1 and 2 for details). The discrepancies of these studies for H_2 were found[4,5] and remain unresolved in these particular regions. Most studies of high-energy electron scattering reported the difference $\Delta N^{\mathrm{el}}(K)$ at each value of K. The DCS at small K (near zero) cannot be accurately evaluated from the computed difference function due to the large roundoff error resulting from the limited precision of the digital computer and the limited number of digits tabulated in published wave functions. In the present work a simple expression for calculating the cross section by an expansion method is derived. This method calculates the cross section to an accuracy equivalent to the given wave function. The DCS for the elastic scattering at high incident electron energies and at very small scattering angles provides the major[6] contribution to the total elastic cross section. Therefore, accurately computed DCS's at small scattering angles are essential in order to obtain the total elastic cross section accurately. There is no N_2 wave function as accurate as the H_2 wave function. However, we use the multiconfiguration self-consistent-field first-order configuration-interaction (MCSCF-FOCI) wave function for N_2 obtained by Stevens.[7] This wave function gives a molecular binding energy of 8.59 eV. It also gives an accurate total electronic energy and quadrupole moment better than the values given by the near-Hartree-Fock (near-HF) wave function of Cade *et al.*[8] (see Table I for comparison). Atomic units are used in tables and figures unless another unit is explicitly indicated. This wave function was successfully used[7] in describing the elastic scattering for low incident electron energies; it is expected to be successful also for high-energy electron scattering. A program has been written to calculate the DCS for the elastic scattering for all scattering angles using the molecular wave function expanded by extensive bases of Slater-type functions (STF). The differential and total elastic cross sections for N_2 can be computed using this correlated wave function and both are given for comparison with experimental data.[17–20]

The scattering of fast electrons by molecular hydrogen is one of the simplest electron-molecule scattering processes. Recently, accurate theoretical and experimental studies for the total scattering intensity for H_2 led to the conclusion that the discrepancy between theory and experi-

TABLE I. One-electron properties for H_2 ($^1\Sigma_g^+$).

WFS	R (a_0)	$-E$ (hartree)	$Q_2(R)$[a]	$Q_4(R)$[b]	$\frac{d\sigma^{el}}{d\Omega}$ ($\theta=0°$)	β	γ
2H	∞	1.000			4.0000		
IAM	1.4	1.000 113 7			4.0000		
LCAO-MO[c] ($\xi=1$)	1.4	1.120 000	0.4529		3.9146		
LCAO-MO ($\xi=1.1895$)	1.4	1.128 188	0.4264	0.1775	1.9308	−1.3208	0.562 56
Wang[d]	1.406	1.138 991	0.3404		2.107		
FB[e]	1.40	1.169 727			2.107		
SCF-DJ[f]	1.4009	1.133 624	0.6645	0.3141	1.9530	−1.404	0.641 84
SCF-Liu[g]	1.40	1.133 616	0.6502		1.9468		
SCF-RK[h]	1.4	1.133 629	0.6634		1.9498		
CI-DJ[f]	1.4009	1.173 032	0.6190	0.2950	1.8989	−1.3472	0.606 72
CI-HS[i]	1.400	1.173 128	0.6419	0.3126	1.8932		
CI-Liu[g]	1.400	1.173 70	0.6004		1.9005		
RK[h]	1.40	1.173 60	0.6257		1.8919		
KW[j]	1.40	1.174 474	0.6155	0.2826[o]	1.8992		
FB[k]					1.947		
CI-Liu[g]	1.449	1.160 32			1.96[q]		
KW[l]	1.4487	1.164 022	0.6510		1.96[q]		
KW[m]	1.4487	1.164 006	0.6600		1.96[q]		
Expt.		1.164 022	0.6379±0.312		1.99±0.20 ($K=0.4$ a.u.)[p] 1.76 (theory at $K=0.4$ a.u.)[p]		

[a] $Q_2(R)=\frac{1}{2}(R^2-6\langle z^2\rangle+2\langle r^2\rangle)\times 1.344\,92\times 10^{-26}$ esu cm^2. The values are tabulated in units of 10^{-26} esu cm^2.

[b] $Q_4=\frac{1}{8}R^4-2\langle P_4(\cos\theta)r^4\rangle$ in a.u.

[c] Linear combination of atomic orbitals and molecular orbitals (LCAO-MO).

[d] See Ref. 42.

[e] See Ford and Browne (FB), Ref. 39.

[f] See Ref. 44.

[g] See Ref. 45.

[h] See Kolos and Roothaan (RK), Ref. 46.

[i] See Ref. 43.

[j] See Ref. 47.

[k] See Ref. 39.

[l] See Ref. 48.

[m] See Ref. 49.

[n] See Ref. 51 for details.

[o] See Ref. 50.

[p] The values for $d\sigma^{el}/d\Omega$ at small scattering angles were reported in Ref. 37 (also private communication).

[q] The values of $\langle R^2\rangle$ and $\langle R^4\rangle$ are 2.1271 and 4.7680 a.u., respectively. Notice that the value $\langle(\langle r^4\rangle)^2\rangle_{\text{vib}}$ is approximately to the value $(\langle r^2\rangle_{\text{vib}})^2$ and so on for the other vibrationally averaged product of the moments.

ment at large scattering angles remains unresolved.[21–23] Structure determination by electron diffraction in the gas phase is based on the validity of first Born theory. Therefore it is quite important to investigate other molecules such as N_2 to see if there is a discrepancy at large scattering angles. Since there are more accurate experimental data[24,25] available and the vibrational effect on $\Delta N(K)$ was shown[26] to be very small, the study of N_2 is a good choice for both theoretician and experimentalist. The difference functions $\Delta N(K)$ (elastic and/or inelastic) for N_2 in the first Born approximation has been calculated on several occasions.[27–31] The molecular wave functions, available up to now from the contracted Gaussian-type function (CGTF) only, have less than 65% electronic correlation energy. The total difference function was calculated[30] and compared with accurate experimental data[25] obtained at incident energies above 37 keV. The agreement is still not good at K around 2 a.u. This may be mainly due to the lack of atomic correlation in their[30] molecular wave functions. It has been shown elsewhere[3] that the comparison of the difference function between theory and experiment is very effective because it can demonstrate the direct connection between the molecular binding energy and the scattering intensity. The following difference functions used in the literature are defined[3] for a homonuclear diatomic molecule:

$$\Delta N^{el}(K)=N^{el}(K)-N^{el}_{\text{IAM}}(K)\ ,$$

$$\Delta N^{inel}(K)=\mathscr{S}(K)-2S(K)\ ,$$

$$\Delta N^{tot}(K)=\Delta N^{el}(K)+\Delta N^{inel}(K)\ ,$$

where $N^{\mathrm{el}}(K)$ and $N_{\mathrm{IAM}}^{\mathrm{el}}(K)$ are defined as follows, with IAM denoting the independent-atom model,

$$N^{\mathrm{el}}(K)=\frac{a^2K^4}{4}\frac{d\sigma^{\mathrm{el}}}{d\Omega}-2Z^2 ,$$

$$N_{\mathrm{IAM}}^{\mathrm{el}}(K)=2[Z-F(K)]^2[1+\sin(KR)/KR]-2Z^2 ,$$

$$N_{\mathrm{IAM}}^{\mathrm{tot}}(K)=N_{\mathrm{IAM}}^{\mathrm{el}}(K)+2S(K) ,$$

where $F(K)$ and $S(K)$ are the x-ray and the incoherent scattering factors for the atom, $\mathscr{S}(K)$ is the molecular incoherent scattering factor, R is the internuclear distance, and Z is the nuclear charge for the separate atom. The $\Delta N_{\mathrm{corr}}^{\mathrm{el}}(K)$ for studying the effect of electron correlation is defined as

$$\Delta N_{\mathrm{corr}}^{\mathrm{el}}(K)=N_{\mathrm{CI}}^{\mathrm{el}}(K)-N_{\mathrm{HF}}^{\mathrm{el}}(K) .$$

The experimental binding energy estimated by high-energy electron scattering is given[3] by

$$b_{\mathrm{expt}}=\frac{1}{2\pi}\int_0^{\infty}\Delta N^{\mathrm{tot}}(K)dK-E_{\mathrm{corr}}+E_{\mathrm{IAM}} ,$$

where E_{IAM} is the binding energy in the IAM and E_{corr} is the sum of the atomic correlation energies. If $N_{\mathrm{IAM}}^{\mathrm{tot}}(K)$ has an electron correlation correction to the separate atoms, then $E_{\mathrm{corr}}=0$, and the difference function $\Delta N^{\mathrm{tot}}(K)$ will not contain the correlation energy contributed from the atomic correlation. A comparison of theory with experiment may not be very informative if theoretical and experimental difference functions contain different amounts of atomic electron correlation. Since the MCSCF-FOCI molecular wave function is not an exact one, the contribution of atomic correlation to both theoretical and experimental $\Delta N^{\mathrm{tot}}(K)$ should be eliminated before the comparison is made. Since there is no accurate experimental measurement of the $\Delta N^{\mathrm{el}}(K)$ at high incident energies, a comparison can only be made between the experimental $\Delta N^{\mathrm{tot}}(K)$ and the computed $\Delta N^{\mathrm{el}}(K)$. Fink *et al.*[24(b)] have done this kind of comparison by using a theory in a HF approximation; the agreement between theory and experiment is very good at K greater than 5 a.u. although the contribution from inelastic scattering is neglected. The theoretical result [with improvement upon $\Delta N^{\mathrm{el}}(K)$ by using a wave function with more electron correlation] is worthwhile to investigate. The effect of electron correlation on the elastic difference function $\Delta N^{\mathrm{el}}(K)$ is also compared with other studies.[29,30,32] Finally, the difference function $\Delta N^{\mathrm{el}}(K)$ calculated using the MCSCF-FOCI wave function is given for comparison with the experimental total difference functions $\Delta N^{\mathrm{tot}}(K)$.[24,25,33,34]

II. THEORY AND COMPUTATIONAL METHOD

The differential cross section for the elastic scattering of electrons by a free-rotating diatomic molecule in the first Born approximation can be written[3,21,23,26–32] as

$$\frac{d\sigma^{\mathrm{el}}}{d\Omega}=\frac{4}{a^2K^4}[Z_A^2+Z_B^2+2Z_AZ_B\sin(KR)/KR$$
$$-F_{\mathrm{ne}}(K)+F_{\mathrm{coh}}(K)] , \tag{1}$$

where ne denotes the electron-nuclear interference and coh the coherent term and

$$F_{\mathrm{ne}}(K)=Z_A\int\sum_{i=1}^{n}\langle\Psi_0|(e^{i\mathbf{K}\cdot\mathbf{r}_{iA}}+e^{-i\mathbf{K}\cdot\mathbf{r}_{iA}})|\Psi_0\rangle\frac{d\Omega_K}{4\pi}$$
$$+Z_B\int\sum_{i=1}^{n}\langle\Psi_0|(e^{i\mathbf{K}\cdot\mathbf{r}_{iB}}+e^{-i\mathbf{K}\cdot\mathbf{r}_{iB}})|\Psi_0\rangle\frac{d\Omega_K}{4\pi} ,$$

$$F_{\mathrm{coh}}(K)=\int\left|\sum_{i=1}^{n}\langle\Psi_0|e^{i\mathbf{K}\cdot\mathbf{r}_i}|\Psi_0\rangle\right|^2\frac{d\Omega_K}{4\pi} .$$

Here Ψ_0 is the ground state of the target wave function for diatomic molecules, Z_A and Z_B are the nuclear charges for atom A and atom B, respectively, and n is the total number of electrons in the target. It is well known that $K=2k_0\sin(\theta/2)$, where k_0 is the incident electron momentum and θ is the scattering angle. In order to accurately compute the DCS at our near zero scattering angle, an expression for the cross section can be written in terms of the various moments as follows. By choosing the internuclear distance vector along the z axis, expanding $\exp(i\mathbf{K}\cdot\mathbf{r})$ and $\exp(i\mathbf{K}\cdot\mathbf{R})$ in power series of $\mathbf{K}\cdot\mathbf{r}$ and $\mathbf{K}\cdot\mathbf{R}$, and averaging $\mathbf{K}$ with respect to $\mathbf{r}$ and $\mathbf{R}$, the differential cross section in Eq. (1) can be rewritten for a homonuclear diatomic molecule as

$$\frac{d\sigma^{\mathrm{el}}}{d\Omega}=\alpha+\beta K^2+\gamma K^4+\cdots , \tag{2}$$

where

$$\frac{d\sigma^{\mathrm{el}}}{d\Omega}(\theta=0^\circ)=\alpha ,$$

$$\alpha/4Z^2=R^4/80-(\langle r^2\rangle+2\langle z^2\rangle)R^2/30$$
$$+(\langle r^2\rangle^2-\tfrac{4}{3}\langle x^2\rangle^2-\tfrac{8}{3}\langle x^2\rangle\langle z^2\rangle)/5 ,$$

$$-\beta/4Z^2=15R^6/8!+(24C_1-6C_2R^2-3C_3R^4/2)7! ;$$

also

$$C_1=\langle r^2\rangle C_4+8\langle x^2\rangle\langle x^4\rangle-8\langle x^2z^2\rangle\langle x^2\rangle$$
$$+4\langle z^2\rangle\langle z^4\rangle-4\langle x^2y^2\rangle\langle z^2\rangle ,$$

$$C_2=C_4+4\langle z^4\rangle-4\langle x^2y^2\rangle ,$$

$$C_3=\langle r^2\rangle+4\langle z^2\rangle ,$$

$$C_4=2\langle x^4\rangle+\langle z^4\rangle+6\langle x^2y^2\rangle+12\langle x^2z^2\rangle ,$$

$$\gamma/4Z^2=(7R^8/32)8!-[R^6(\langle r^2\rangle+6\langle z^2\rangle)/2]9!$$
$$-C_5+C_6-C_7+C_8$$

and

$$C_5=[R^4/(4!)^2]/2(2\langle x^4\rangle/105+\langle z^4\rangle/9+2\langle x^2y^2\rangle/105+4\langle x^2z^2\rangle/21)\,,$$

$$\begin{aligned}C_6=(&76\langle x^4\rangle^2/315+\langle z^4\rangle^2/9+4\langle x^4\rangle\langle z^4\rangle/105+12\langle x^2y^2\rangle^2/35\\&+32\langle x^2z^2\rangle^2/35+16\langle x^2y^2\rangle\langle x^2z^2\rangle/35+8\langle x^4\rangle\langle x^2y^2\rangle/21\\&+16\langle x^4\rangle\langle x^2z^2\rangle/35+4\langle z^4\rangle\langle x^2y^2\rangle/105+8\langle z^4\rangle\langle x^2z^2\rangle/21)/144\,,\end{aligned}$$

$$C_7=(R^2/6!-\langle z^2\rangle/180)[(2\langle x^6\rangle+7\langle z^6\rangle/63+2\langle x^4y^2\rangle+3\langle x^4z^2\rangle+5\langle x^2z^4\rangle+3\langle x^2y^2z^2\rangle)/21]\,,$$

$$C_8=\langle x^2\rangle/90[(8\langle x^6\rangle+\langle z^6\rangle)/63+(8\langle x^4y^2\rangle+6\langle x^4z^2\rangle+4\langle x^2z^4\rangle+6\langle x^2y^2z^2\rangle)/21]\,,$$

where $\langle r^2\rangle$, $\langle x^2y^2\rangle$, etc., are the expectation values of the target wave function. Notice that the charge density $\rho(\mathbf{r})=\Psi_0^*(\mathbf{r})\Psi_0(\mathbf{r})$ is normalized to 1 instead of n [i.e., $\int\rho(\mathbf{r})d\mathbf{r}=1$] in Eq. (2), i.e., $\langle r^2\rangle$, $\langle x^2y^2\rangle$, etc., are written on a per-electron basis in Eq. (2).

According to the theory given by Inokuti and McDowell,[35] the total elastic cross section for a homonuclear diatomic molecule can be written

$$\sigma^{\rm el}=\frac{\pi}{k_0^2}(A+B/k_0^2+C/k_0^4+\cdots) \qquad (3)$$

with

$$A=4\int_0^\infty\{2Z^2[1+\sin(KR)/KR]-F_{\rm ne}(K)+F_{\rm coh}(K)\}\frac{dK}{K^3}\,,$$

where k_0^2 is the incident energy in rydbergs and the constants B, C, etc., in Eq. (3) can be obtained from the electron-atom scattering theory.[35]

To calculate the moments and the Fourier-transformed integral in Eqs. (1) and (2) for a diatomic molecule, the one-electron density function constructed from the STF is transformed into ellipsoidal coordinates and then the Fourier-transform integrals can be computed by using accurate computational techniques.[21,36]

III. RESULTS OF CALCULATION AND COMPARISON WITH EXPERIMENT

A. H_2

The elastic scattering of fast electrons by H_2 has been investigated elsewhere.[3,21,23,37–39,41] The studies for both the DCS and the total cross section for the incident energy from hundreds of electron-volts to 2 keV were also given.[6,40,41] This report only presents a study for the DCS at K near zero and at high incident electron energies. In Table I the DCS at $\theta=0$, as well as other one-electron properties, is given for various H_2 wave functions.[42–49] It is interesting to see that $d\sigma^{\rm el}/d\Omega$ $(\theta=0°)$, calculated using the Kolos-Wolniewicz (KW),[47] configuration-interaction—Liu (CI-Liu),[45] CI—Davidson-Jones (CI-DJ),[44] CI—Hagstrom and Shull (CI-HS)[43] wave functions all converged to one value, 1.90 a.u., although their total molecular binding energies differ by more than 3%. The theoretical DCS's at small scattering angles are calculated according to Eq. (2), where $d\sigma^{\rm el}/d\Omega$ $(\theta=0°)$ includes an adiabatic or nonadiabatic correction due to the KW wave function[48,49] and the constants β and γ are calculated from the DJ[44] wave function. According to Table II, the values for $Q_2(R)$ and $Q_4(R)$ calculated using the CI-DJ and KW wave functions[50] are in agreement to within 5%; consequently the constants β and γ calculated from the CI-DJ wave function would not be in error by more than 5%. Accordingly the cross section calculated using these constants at K less than 0.5 a.u. would not be in error by more than 0.4%. The experimental results would have to have an error less than 0.4% in order to discriminate the DCS calculated using either the KW or the CI-DJ wave function.

There is one experimental DCS accurately reported for very small scattering angles near zero by Geiger[37] at 25 keV incident energy. The absolute DCS's at 2 keV incident energy and at some scattering angles reported by van Wingerden *et al.*[6] are available for comparison with the experimental data reported by Geiger. In Fig. 1, it is shown that they are in relatively very good agreement at $K>1.0$ a.u. The DCS at $K=0.45$ a.u. (for scattering angle of 3° at 1 keV) reported by Fink *et al.*[40] which is renormalized to the data of van Wingerden *et al.*[6] is also shown in Fig. 1. In the first Born theory, this incident energy may be high enough, but it is a valuable small-angle data point to compare with the data reported by Geiger. Since the experimental report by Geiger[37] is not an absolute measurement and the experimental data of van Wingerden *et al.*[6] have been shown[6] to be in good agreement with the first Born theoretical values[21,29] at $K>1.0$ a.u., the experimental data reported by Geiger are scaled relatively at $K>1.0$ a.u. to the theoretical value before the comparison for small-angle scattering is made. In comparison with theory, it is found that the experimental data points and theoretical values are all in good agreement at $1.1>K>0.6$ a.u. but the experimental data at $0.6>K>0.4$ a.u. are slightly underestimated by theory [experimental data reported by Geiger[37] have 10% error at K greater than 0.4 a.u. (private communication[37])]. It is very urgent to have new experimental data with an error less than 10% at very small scattering angles to compare with the theoretical values reported here.

B. N_2

1. *Differential cross section*

In Table II, the values of α $[=d\sigma^{\rm el}/d\Omega\ (\theta=0°)]$, β, and γ in Eq. (2) as well as other one-electron properties of

TABLE II. One-electron properties for $N_2(X\,^1\Sigma_g^+)$.

WF	R (a_0)	$-E$ (hartree)	$Q_2(R)$[a]	$Q_4(R)$[b]	$\frac{d\sigma^{el}}{d\Omega}(\theta=0°)$	β	γ	A[c]
2N(CI)[d]	∞	108.998						130
2N(HF)	2.068	108.802			95.13[r]			
Scherr[e]	2.068	108.634	−1.72		44.12			
Richardson[f]	2.0675	108.7832	−1.40	−3.040	65.29	−56.072	27.313	
Snyder and Basch[g]	2.0741	108.8695	−1.81		62.70			
Vladimiroff[h]	2.068	108.9726	−1.08		63.37			
Dunning[i]	2.079	108.971 86	−1.00[o]		63.37			
Amos[j]	2.074	108.9898	−0.92(1.13)[p]	−7.246(−6.70)[p]	63.08			
Cade *et al.*[k]	2.068	108.9928	−0.95	−6.844	64.35	−57.760	30.011	127
Dunning[l]	2.079	109.104 04	−1.24[o]		62.55[o]			
Stevens[n]	2.068	109.117 12	−1.04	−6.038	61.28	−53.131	26.412	124
Expt.	2.074	109.586[n]	−1.09[q]		54±5[s]			115±12[s]

[a] $Q_2=\frac{1}{2}(7R^2-42\langle z^2\rangle+14\langle r^2\rangle)$ in a.u.

[b] $Q_4=\frac{7}{8}R^4-14\langle r^4P_4(\cos\theta)\rangle$ in a.u.

[c] The values for the constant A are estimated by numerically integrating from $K=0$ to 30 a.u. and the rest of the integral from $K=30$ a.u. to ∞ is approximated by the electron-atom scattering theory, and the constant B in Eq. (3) is equal to −98.

[d] See Ref. 28.

[e] See Ref. 9.

[f] See Ref. 10.

[g] See Ref. 11.

[h] See Ref. 12.

[i] See Ref. 13.

[j] See Ref. 14.

[k] See Ref. 8. 3σ orbital has an occupation number of 1.999 264 according to its tabulated wave function. This lower occupation number will reduce the theoretical values of one-electron properties computed here. Therefore all the values may be good to three-digit accuracy only.

[l] See Ref. 13.

[m] See Ref. 7.

[n] See Ref. 15.

[o] The values are calculated from Table IV in Ref. 13 (GVB extended).

[p] The values in the parentheses are corrected with second-order Moller-Plesset contribution.

[q] See Ref. 16.

[r] $d\sigma^{el}/d\Omega=\frac{4}{9}\langle r^2\rangle^2$, with $\langle r^2\rangle$ taken from F. C. Fischer, At. Data **4**, 301 (1972).

[s] This value is obtained by extrapolation of the experimental data given in Ref. 18.

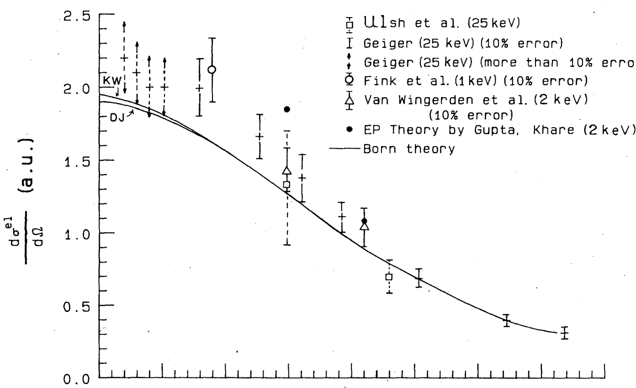

FIG. 1. Differential cross sections for electron scattering of H_2.

calculated using various wave functions[7–14] are given. The quadrupole moment calculated using the MCSCF-FOCI wave function[7] is in excellent agreement with experiments.[16] The multipole moments are also in agreement with other calculations.[13,14] In Table III, the DCS's computed according to Eq. (1) and Eq. (2) are given for comparison. It is shown that the values calculated from Eq. (1) have a significant roundoff error due to the limited precision of digital computers and the limited number of digits of the reported wave function. The values at scattering angles near zero can be accurately evaluated only by Eq. (2). The value calculated according to Eq. (2) using the wave function of Cade *et al.*[8] are also recomputed here for a few small momentum transfers to compare with the values reported by Epstein and Stewart.[28] Their values are shown to be in good agreement with the present calculation. Three sets of theoretical values calculated using the self-consistent field (SCF),[10] near-HF,[8] and MCSCF-FOCI (Ref. 7) wave functions, are given in Table IV. It is shown that the effect of electron correlation on

TABLE III. Comparison of calculations using Eqs. (1) and (2) for the DCS for $N_2(X^1\Sigma_g^+)$.

	MCSCF-FOCI				Near-HF						
K (a_0^{-1})	$F_{ne}(K)$	$F_{coh}(K)$	$\frac{d\sigma^{el}}{d\Omega}$	$\frac{d\sigma^{el\,a}}{d\Omega}$	$F_{ne}(K)^b$	$F_{ne}(K)^c$	$F_{coh}(K)^b$	$F_{coh}(K)^c$	$\frac{d\sigma^{el\,c}}{d\Omega}$	$\frac{d\sigma^{el\,b}}{d\Omega}$	$\frac{d\sigma^{el\,a,b}}{d\Omega}$
0.0097						13.999		195.98			64.36
0.0484	13.979 21	195.581 46	307.74	61.16	13.978 98		195.589 43				64.23
0.0967	13.917 05	194.330 86	60.84	60.79	13.916 15	13.916	194.305 58	194.30		63.82	63.83
0.1451	13.814 21	192.268 07	60.18	60.18	13.812 21		192.212 19			63.13	63.17
0.1934	13.671 80	189.423 63	59.33	59.33	13.668 30	13.668	189.326 71	189.33	95.72	62.25	62.25
0.2418	13.491 33	185.839 55	58.26	58.27	13.486 00		185.692 86			61.09	61.10
0.2901	13.274 71	181.567 86	56.99	57.00	13.267 28	13.267	181.364 67	181.36	61.49	59.71	59.72
0.3385	13.024 19	176.669 20	55.53	55.54	13.014 45		176.405 02			58.12	58.14
0.3868	12.742 35	171.211 29	53.89	53.92	12.730 16	12.730	170.883 94	170.88	56.46	56.36	56.40
0.4352	12.431 98	165.267 24	52.11	52.17	12.417 30		164.876 87			54.43	54.50
0.4836	12.096 14	158.913 71	50.19	50.30	12.078 97	12.079	158.462 66	158.46	52.10	52.36	52.50

[a] By the expansion method.

[b] From the present calculation, where the total number of electrons is renormalized exactly equal to 14 and $\alpha=64.37$, $\beta=57.779$, $\gamma=30.020$.

[c] Calculation based on the values of F_{ne} and F_{coh} tabulated in Ref. 28.

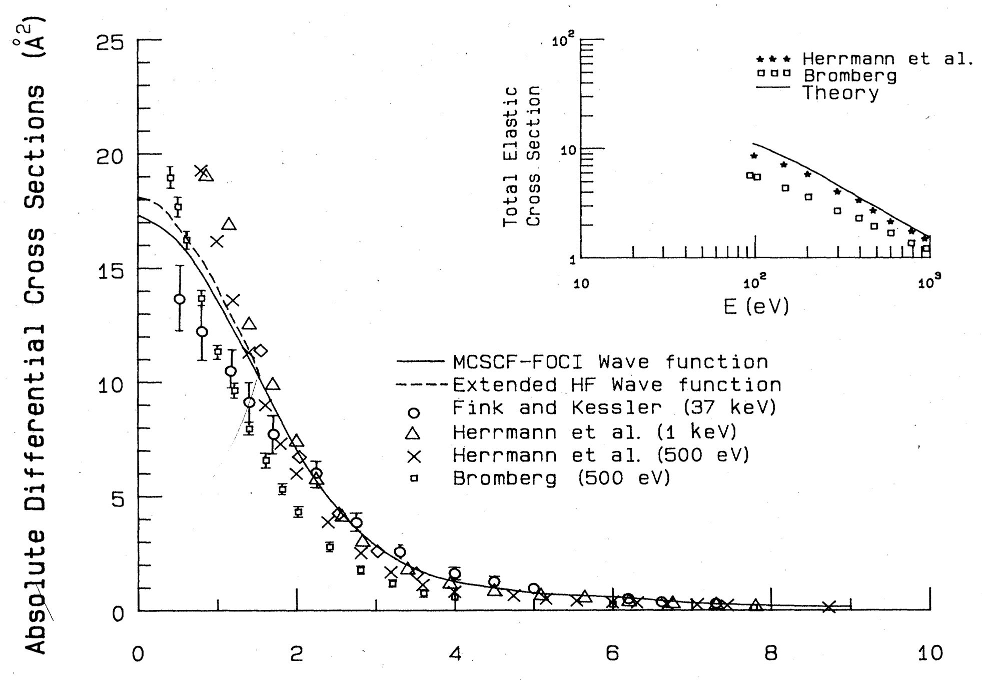

FIG. 2. Differential cross sections for electron scattering of N_2.

the DCS is very important, it contributes a 6% difference at $K=0$. In Fig. 2, the experimental data and theoretical values are shown for comparison. The values at small scattering angles calculated using the MCSCF-FOCI wave function are shown to be in much better agreement with the experimental data[18] at 37 keV [the relativistic correction to the DCS, $(1-v^2/c^2)^{-1}(d\sigma/d\Omega)_{\text{nonrel}}^{\text{Born}}$, where v is the incident electron velocity, has been neglected]. The experimental data are overestimated by theory from $K=0$ to 2 $\mathring{A}^{-1}$ and underestimated by theory from $K=3$ to 5 $\mathring{A}^{-1}$. However, with the relativistic correction to the data at 37 keV (17%), the theory and the experiment are not in good agreement over all the K range. The experimental data[17] of relative measurements at 40 keV by the photographic recording method are in good agreement with the theoretical values over the range of K from 3 to

TABLE IV. The DCS and the difference function for $N_2(X\,^1\Sigma_g^+)$.

	MCSCF-FOCI		HF		SCF	
$\frac{1}{2}KR$	$\frac{d\sigma^{el}}{d\Omega}$	$\Delta N^{el}(K)$	$\frac{d\sigma^{el}}{d\Omega}$	$\Delta N^{el}(K)^a$	$\frac{d\sigma^{el}}{d\Omega}$	$\Delta N^{el}(K)^a$
0.0000	61.2837	0.0000	64.3503	0.0000	65.2915	0.0000
0.1000	60.7891	−0.0001	63.8127	0.0001	64.7692	0.0004
0.1500	60.1773	−0.0004	63.1480	0.0005	64.1230	0.0008
0.2000	59.3329	−0.0014	62.2314	0.0004	63.2309	0.0008
0.2500	58.2681	−0.0034	61.0764	−0.0004	62.1055	0.0004
0.3000	56.9907	−0.0070	59.9801	−0.0011	60.9431	0.0006
0.3500	55.5261	−0.0126	58.3156	−0.0013	59.3336	0.0021
0.4000	53.8896	−0.0209	56.4956	−0.0015	57.5777	0.0046
0.4500	52.1058	−0.0323	54.5354	−0.0029	55.6784	0.0073
0.5000	50.1887	−0.0470	52.4453	−0.0065	53.6424	0.0099
0.5500	48.1639	−0.0647	50.2500	−0.0116	51.4929	0.0133
0.6000	46.0538	−0.0856	47.9723	−0.0165	49.2521	0.0199
0.6500	43.8809	−0.1104	45.6356	−0.0225	46.9428	0.0287
0.7000	41.6668	−0.1398	43.2627	−0.0320	44.5876	0.0379
0.7500	39.4324	−0.1742	40.8759	−0.0452	42.2085	0.0474
0.8000	37.1975	−0.2127	38.4959	−0.0614	39.8263	0.0583
0.8500	34.9802	−0.2539	36.1420	−0.0798	37.4604	0.0715
0.9000	32.7972	−0.2970	33.8315	−0.1002	35.1285	0.0868
0.9500	30.6632	−0.3425	31.5796	−0.1236	32.8464	0.1032
1.0000	28.5912	−0.3912	29.3998	−0.1515	30.6280	0.1186
1.1000	24.6752	−0.4995	25.2979	−0.2250	26.4280	0.1390
1.2000	21.1145	−0.6098	21.5896	−0.3174	22.6002	0.1438
1.3000	17.9459	−0.7229	18.3077	−0.4173	19.1860	0.1350
1.4000	15.1816	−0.8378	15.4591	−0.5320	16.2005	0.0955
1.5000	12.8134	−0.9589	13.0300	−0.6436	13.6373	0.0345
1.6000	10.8181	−1.0671	10.9916	−0.7488	11.4734	−0.0516
1.7000	9.1623	−1.1612	9.3056	−0.8376	9.6747	−0.1558
1.8000	7.8066	−1.2475	7.9288	−0.9061	8.2002	−0.2743
1.9000	6.7092	−1.2963	6.8164	−0.9426	7.0062	−0.3918
2.0000	5.8290	−1.3154	5.9248	−0.9389	6.0489	−0.4937
2.2000	4.5681	−1.2683	4.6469	−0.8386	4.6820	−0.6453
2.4000	3.7613	−1.0760	3.8264	−0.5926	3.8165	−0.6471
2.6000	3.2177	−0.7630	3.2703	−0.2540	3.2439	−0.4963
2.8000	2.8129	−0.4048	2.8544	0.1317	2.8269	−0.2110
3.0000	2.4750	−0.0344	2.5069	0.5022	2.4848	0.1446
3.2000	2.1679	0.2805	2.1919	0.7854	2.1768	0.4770
3.4000	1.8784	0.4900	1.8961	0.9658	1.8870	0.7420
3.6000	1.6050	0.6133	1.6179	1.0293	1.6130	0.8990
3.8000	1.3516	0.6175	1.3607	0.9797	1.3585	0.9332
4.0000	1.1230	0.5459	1.1293	0.8550	1.1286	0.8737
4.2000	0.9229	0.4263	0.9272	0.6715	0.9273	0.7353
4.4000	0.7533	0.2678	0.7560	0.4606	0.7564	0.5525
4.6000	0.6137	0.1375	0.6153	0.2591	0.6159	0.3671
4.8000	0.5021	0.0132	0.5030	0.1021	0.5035	0.2181
5.0000	0.4153	−0.0499	0.4157	−0.0290	0.4162	0.0898
5.2000	0.3492	−0.0977	0.3493	−0.0954	0.3497	0.0223
5.4000	0.2998	−0.1143	0.2997	−0.1204	0.3001	−0.0083
5.6000	0.2629	−0.0852	0.2628	−0.1320	0.2630	−0.0301
5.8000	0.2351	−0.0311	0.2349	−0.1095	0.2351	−0.0223
6.0000	0.2132	0.0201	0.2131	−0.0501	0.2131	0.0179
6.4000	0.1790	0.0918	0.1789	0.0522	0.1788	0.0738
6.8000	0.1494	0.1163	0.1493	0.0929	0.1492	0.0708
7.2000	0.1214	0.1063	0.1214	0.0864	0.1212	0.0367
7.6000	0.0962	0.0550	0.0962	0.0529	0.0960	−0.0063
8.0000	0.0759	0.0302	0.0758	−0.0197	0.0757	−0.0778
8.4000	0.0612	0.0348	0.0612	−0.0223	0.0611	−0.0799
8.8000	0.0516	0.0395	0.0516	0.0394	0.0515	−0.0271
9.2000	0.0454	0.0582	0.0453	0.0591	0.0453	−0.0239
9.6000	0.0405	0.0721	0.0405	0.0731	0.0404	−0.0263

TABLE IV. (*Continued*).

$\frac{1}{2}KR$	MCSCF-FOCI $\frac{d\sigma^{el}}{d\Omega}$	MCSCF-FOCI $\Delta N^{el}(K)$	HF $\frac{d\sigma^{el}}{d\Omega}$	HF $\Delta N^{el}(K)^a$	SCF $\frac{d\sigma^{el}}{d\Omega}$	SCF $\Delta N^{el}(K)^a$
10.0000	0.0359	0.0736	0.0359	0.0878	0.0358	−0.0208
11.0000	0.0243	0.0913	0.0243	0.0505	0.0242	−0.0396

[a] The IAM are taken from the value of HF tabulated in C. Tavard, D. Nicholas, and M. Rouault, J. Chim. Phys. **64**, 540 (1967).

5 Å^{-1}. The experimental data at 1 keV reported by Herrmann *et al.*[19] are also shown to be in relatively good agreement with the theoretical values at K greater than 2 Å^{-1}. Due to the fact that the agreement between theory and experiment for other one-electron properties, such as the quadrupole moment, is excellent, the disagreement for the DCS at large scattering angles at incident energy of 37 keV is unlikely to be due to the inadequacy of electron correlation in the target wave function; it requires further experimental studies. At 37 keV incident energy, the disagreement at small K may still be due to the insufficient electron correlation of the MCSCF-FOCI wave function because the theoretical values lie above the experimental values which is contrary to the study of H_2 given in Sec. III A. Nevertheless, further experimental data with a better precision will help to confirm the accuracy of the early experimental study,[18] where the data were reported with an error of 10% [quoted in Ref. 17 and 24(b)]. At incident energies below 1 keV, the disagreement between theory and experiment at small scattering angles is mainly due to the failure of the first Born theory which has been reported[41] in the study of H_2.

2. *Difference function* $\Delta N(K)$

The effect of electron correlation due to the inelastic scattering can be examined as follows. The effect of electron correlation on $F(K)$ and $S(K)$ for the nitrogen atom was shown[51,52] to be very important especially for $S(K)$ ranging from $K=0$ to 4 a.u. There is more than 50% correlation energy, i.e., E_{corr} due to the atomic correlation in N_2. However, if we follow the method proposed in the introduction for comparison between theory and experiment, the effect of correlation resulting from the atomic correlation can be totally eliminated. It means that the effect of electron correlation on $\Delta N^{tot}(K)$ due to the inelastic scattering will be substantially reduced.

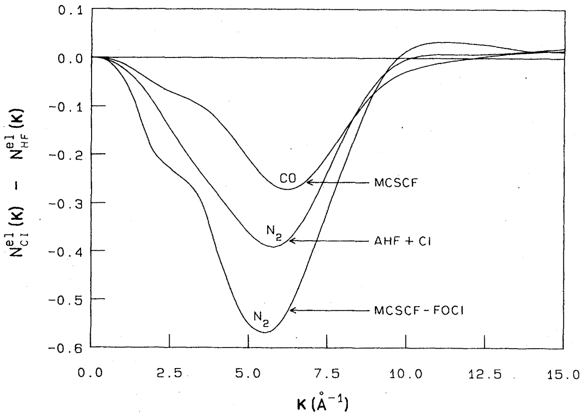

FIG. 3. Effect of electron correlation on $\Delta N^{el}(K)$, i.e., $\Delta N^{el}_{corr}(K)=N^{el}_{CI}(K)-N^{el}_{HF}(K)$ for various wave functions.

The effect of electron correlation on $N^{el}(K)$ for diatomic molecules was shown[30,32] to be very important over a wide range of K. In Fig. 3, the effect of electron correlation on the difference function is shown in terms of the difference $\Delta N^{el}_{corr}(K)$ and the effect is shown to be very important for K from 0 to 5 a.u. The $\Delta N^{el}_{corr}(K)$ calculated for N_2 using molecular orbitals expanded by the STF and the CGTF are all shown to be most noticeable around 3 a.u. although they differ in magnitude. For another close-shell 14-electron system such as CO, it is also shown[32] to have similar characteristic differences over all K. It is interesting to learn that $\Delta N^{el}(K)$ calculated using the MCSCF-FOCI wave function giving 27% correlation energy (below its molecular HF energy level) is surprisingly more effective than the one reported[30] by using the approximate HF-CI wave function giving 46% correlation energy. Notice that the DCS's, calculated using a highly correlated wave function (total energy equal to −109.1512 Hartree) reported by Hirota *et al.*[29] are very similar to the values calculated using the near-HF wave function. This may be due to their wave function containing no d-shell correlation. There are no general criteria to assess the overall quality of a wave function, but it is believed that a wave function which gives better multipole moments in addition to its total energy may be a good one for the study of one-electron properties such as the DCS for the elastic scattering.[53] According to the study of these properties for N_2 (shown in Table II) and for H_2 (shown in Table I), the one-electron density obtained from MCSCF-FOCI wave function is believed to be sufficiently accurate to calculate the DCS for the elastic scattering. The nitrogen-atom scattering factors calculated by Tanaka and Sasaki[54] are used to calculate the IAM, because both the atomic wave function and the MCSCF-FOCI molecular wave function are constructed from the same STF bases. The vibrational correction to the difference function for N_2 can be neglected[26] because it is less than 0.5%. The experimental $\Delta N^{tot}(K)$ is taken for comparison from the one obtained by matching the full correlated IAM to the experiment at small K [Fig. 9 in Ref. 24(b)]. One set of experimental data[34] containing atomic correlation which agrees well with other data sets[25,33] is shown in Fig. 4 for

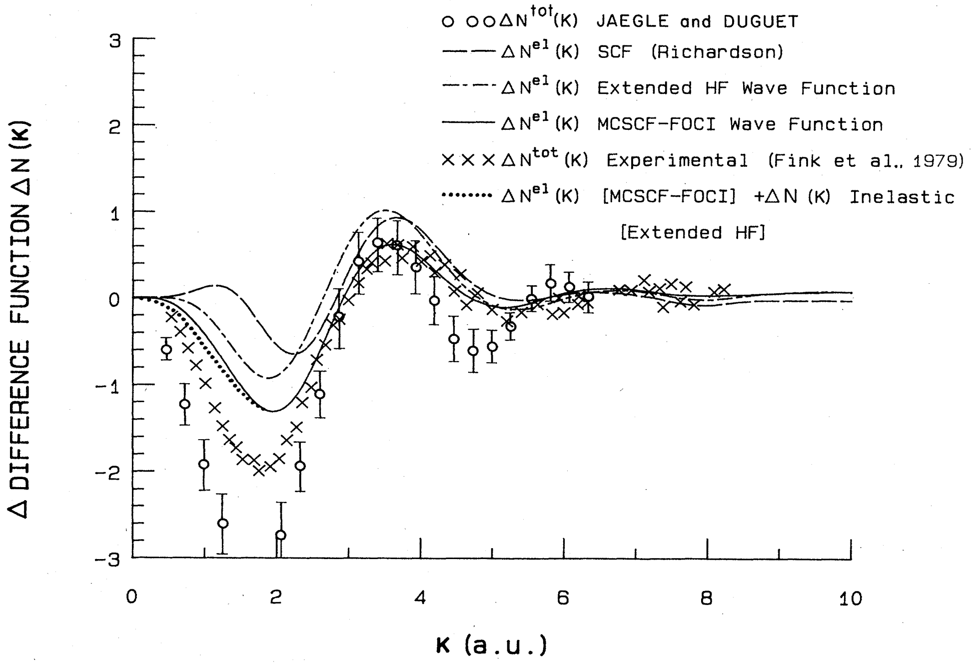

FIG. 4. Comparison of the experimental $\Delta N^{\mathrm{tot}}(K)$ vs the theoretical $\Delta N^{\mathrm{el}}(K)$.

comparison with the data from Ref. 24(b). In Fig. 4, it is shown that the total experimental[24(b)] difference function $\Delta N_{\mathrm{expt}}^{\mathrm{tot}}(K)$ for K from 2.5 to 8 a.u. is in excellent agreement with theoretical values $\Delta N^{\mathrm{el}}(K)$ calculated using the MCSCF-FOCI wave function and the correlated atomic scattering factors given by Tanaka and Sasaki.[54] However, the values calculated from the near-HF wave function[8] are not in agreement with the experiment when K is less than 5 a.u. The $\Delta N^{\mathrm{el}}(K)$ in the HF approximation may be only valid at K larger than 5 a.u. An early calculation[27] of $\Delta N^{\mathrm{tot}}(K)$, which used the molecular SCF wave function[10] and the IAM with no electron correlation, shows the same behavior as described above. Recently the total difference function was calculated[30] using an approximate HF-CI wave function (with 62% correlation energy) expanded from the CGTF. It is shown that theory and experiment are in very good agreement at large K. From both studies there is no observed discrepancy within the experimental uncertainty for N^2 at large K as the one reported in the study of H_2.

3. *Total elastic cross section*

The constant A, defined in Eq. (3), calculated using various wave functions is given in Table II. The computed total elastic cross section according to Eq. (3) is shown in Fig. 2. The experimental DCS for large momentum transfers at either 1 keV or 500 eV incident energy are not in good agreement with the present theoretical value. However, the total cross sections for the incident energies from 100 eV to 1 keV reported by Herrmann *et al.*[19] is in very good agreement with the theoretical values reported here. It is shown that the experimental results from Bromberg[20] are not in good agreement with the present calculation. The theory given by Inokuti and McDowell[35] is remarkably good for N_2 even when the incident energy goes as low as the hundred-electron-volt range. The study of the total cross section reported by van Wingerden *et al.*[6] for H_2 shows that the experimental data within their experimental error at incident energies above 600 eV are all in good agreement with the theory given by Inokuti and McDowell. The less-accurate differential cross sections[39] were used in obtaining the constant A in Eq. (3). It is concluded that the effect of correlation on the total cross section is shown to be not very important for diatomic molecules such as N_2 and H_2. This is in agreement with studies[35] on atoms.

IV. DISCUSSIONS AND CONCLUSIONS

The description of one-electron properties given by different types of wave functions for diatomic molecules, N_2 and H_2, is studied in great detail here. According to Table II, the quadrupole moment and $d\sigma^{\mathrm{el}}/d\Omega$ $(\theta=0^\circ)$ calculated using the generalized valence bond (GVB) CI wave function expanded by the CGTF given by Dunning *et al.*[13] are in very good agreement with the values calculated using the MCSCF-FOCI wave function. Both wave functions give about the same amount of total energy. The discrepancies found in the DCS at very small scattering angles, from 8 to 15 mrad at 25 keV incident electron energy are not well understood for H_2. However, notice that the data for scattering angles less than 8 mrad may not be measurable because of shadow scattering.[55] The discrepancy is very similar to the ones found in the studies of Compton scattering[4] and $(e,2e)$ reaction spectroscopy.[5] Those discrepancies remain unresolved for H_2. However, there are no such discrepancies for He in all the studies[56] mentioned above. The discrepancy found at small scattering angles for N_2 may be due to the inadequacy of the correlated wave function used here, because the wave function includes only first-order configuration-interaction corrections. But it calls for new experimental data for both N_2 and H_2 to clarify all the discrepancies discovered in this work. The discrepancies for $\Delta N^{\text{tot}}(K)$ at large scattering angles are not observed here for N_2. However, the experimental data at large scattering angles shown in Fig. 4 have a large uncertainty. It needs to be improved in order to compare both theoretical values reported here and in Ref. 30. More importantly, new accurate experimental data for the elastic scattering at very high incident energy are definitely needed to confirm the conclusion drawn above.

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