

LETTER TO THE EDITOR

**Theoretical evidence for quasi-molecular structure at small internuclear distances in elastic ion-atom scattering†**

H Hartung, B Fricke, W-D Sepp, W Sengler and D Kolb

Department of Physics, University of Kassel, D-3500 Kassel, West Germany

Received 6 March 1985

**Abstract.** The potential energy curve of the system Ne-Ne is calculated for small internuclear distances from 0.005 to 3.0 au using a newly developed relativistic molecular Dirac-Fock-Slater code. A significant structure in the potential energy curve is found which leads to a nearly complete agreement with experimental differential elastic scattering cross sections. This demonstrates the presence of quasi-molecular effects in elastic ion-atom collisions at keV energies.

The calculation of interatomic potentials to describe atomic scattering processes has a long history (see e.g. Torrens 1972). The main theoretical difficulty in calculating realistic potential energy surfaces is, of course, the complexity of the many-particle problem for such a system, which, in addition, for heavy systems has to include relativity. Up to now no detailed calculations exist for many-electron potentials with internuclear separations  $R < 1$  au. The usual methods to describe this problem are based on the statistical energy expression (see e.g. Gombas 1956, Kohn and Sham 1965) for the total energy with a superposition of two unperturbed atomic charge densities (Nikulin 1971, Wilson and Bisson 1971, Gärtner and Hehl 1979, Loftager *et al* 1979, Loftager and Kristensen 1981, Hartung *et al* 1982, Hartung and Fricke 1983). The results of such calculations with two atomic Hartree-Fock-Slater charge densities (Nikulin 1971, Gärtner and Hehl 1979, Loftager *et al* 1979, Loftager and Kristensen 1981, Hartung *et al* 1982, Hartung and Fricke 1983) lead to some correspondence between atomic inner-shell interaction and measured structures in the elastic scattering cross sections. Small-angle scattering experiments, carried out by Loftager *et al* (1979) and Loftager and Kristensen (1981) at impact energies from a few to some hundred keV, however, show that there are still systematic deviations.

We approach the same problem with a newly developed relativistic molecular self-consistent field Dirac-Fock-Slater (SCF-D<sub>FS</sub>) code (for details see Sepp *et al* 1984). This code might later be improved by a molecular *g*-Hartree method which has been proposed for atomic systems by Dietz and Weymans (1984a, b). To get a good representation of the wavefunctions for all internuclear distances  $R$  we selected numerical Dirac-Fock-Slater atomic wavefunctions as basis functions. Apart from those of the separated atoms we included SCF wavefunctions calculated in the monopole part of the nuclear potential of the molecule, and additional s, p and d functions from higher- $Z$  atoms. As a main result of these calculations we obtain the total energy  $E_M(R)$  as a function of the internuclear distance  $R$ . In subtracting the total energies

† Supported by Gesellschaft für Schwerionenforschung (GSI), Darmstadt.

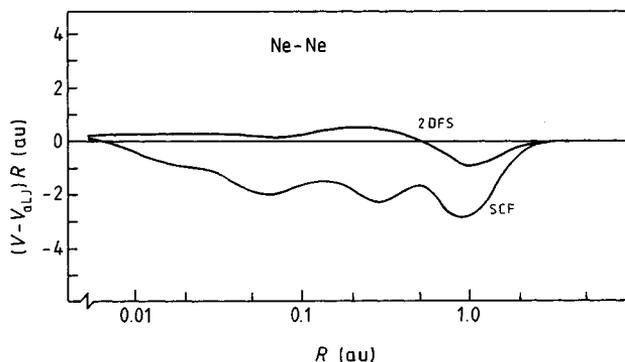
$E_A$  of the two separate scattering partners from atomic calculations we get the interatomic potential

$$V(R) = E_M(R) - E_{A_1} - E_{A_2}.$$

The total exchange potential is given by

$$V_{\text{ex}} = -\frac{3}{2}\alpha_x \left( \frac{3}{\pi} \rho(\mathbf{r}, R) \right)^{1/3}$$

with the Slater exchange parameter  $\alpha_x$ , and the total electron density  $\rho$ . We chose  $\alpha_x = 0.7$  for the molecular calculation in accordance with the proposal by Dunlap *et al* (1979) as well as Becke (1982) and Laaksonen (1983), as no consistent choice of  $\alpha_x$  exists for molecules which would be comparable with the  $\alpha_x$  values for atoms by Schwarz (1972). The resulting potential energy curve for the system Ne-Ne is shown in figure 1. To visualise the molecular structure effect it is useful to plot the scaled potential  $[V(R) - V_{\text{aLJ}}(R)]R$  on a logarithmic  $R$  scale.  $V_{\text{aLJ}}(R)$  is the average Lenz-Jensen potential for Ne-Ne, as suggested by Loftager *et al* (1979). The curve designated SCF results from our relativistic Dirac-Fock-Slater code, while the 2DFS curve is calculated with the statistical method according to Hartung and Fricke (1983), using as total electron density the sum of two relativistic atomic Dirac-Fock-Slater (DFS) densities at the internuclear separation  $R$ . The 2DFS curve also represents our choice for the first iteration in the SCF calculation. While the 2DFS curve has a rather weak structure, the SCF potential energy curve shows stronger binding for all distances, and has a much more detailed structure.



**Figure 1.** Interatomic potential energy curves for Ne-Ne relative to the average Lenz-Jensen potential (Loftager *et al* 1979). 2DFS, statistical energy calculation using relativistic atomic densities, SCF, relativistic quasi-molecular calculation.

The difference between the two curves is due to the electron density of the molecular system compared with the two undisturbed atomic charge densities. The re-arrangement of the electrons, which is not allowed in the 2DFS case, leads to a general lowering of the total energy. The SCF curve represents the adiabatic approximation for the scattering process, while the 2DFS curve represents the sudden approximation.

For the SCF potential energy curve it is also possible to try to interpret the additional structures in terms of the single-particle adiabatic correlation diagram of this system shown in figure 2, where we plotted the energy eigenvalues from the calculations as

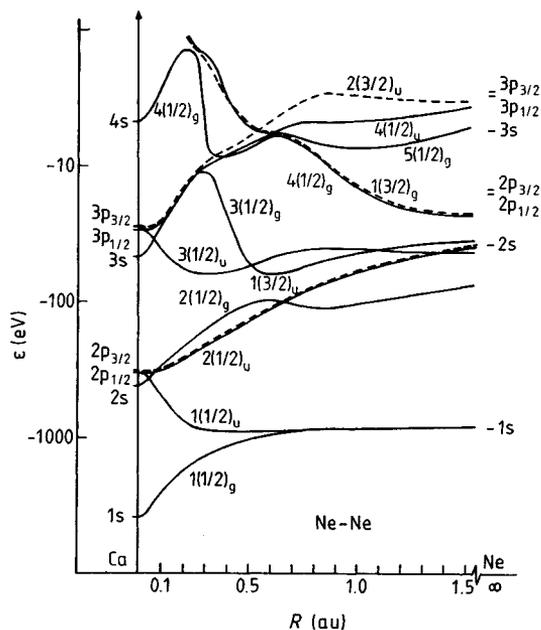
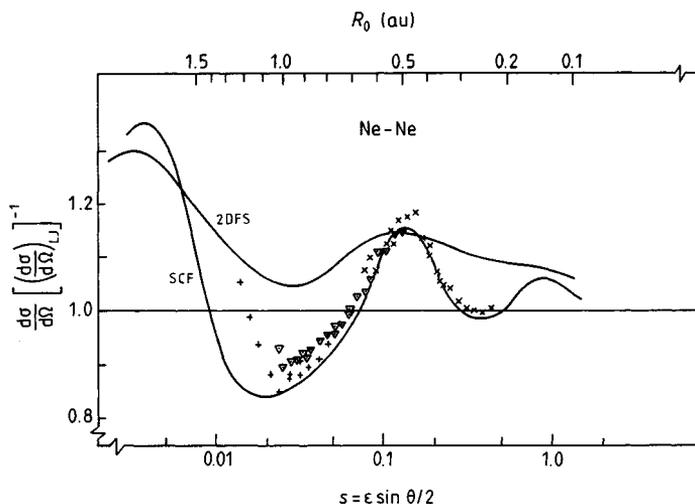


Figure 2. Relativistic Dirac-Fock-Slater correlation diagram for Ne-Ne.

a function of the internuclear distance. The full curves correspond to  $m_j = \frac{1}{2}$  states; the broken curves indicate  $m_j = \frac{3}{2}$  states. The innermost  $R$  value calculated here is 0.005 au. We find three internuclear distances where isolated minima for occupied molecular levels occur. The  $2(1/2)_g$  level has an isolated minimum at about 0.85 au with a depth of about 15 eV. As the level is doubly occupied this produces a relative binding contribution of about 30 eV, which can be seen in the potential energy curve in figure 1 at the same value of  $R$ . Similar arguments can be given for the minima of the  $1(1/2)_u$  and  $3(1/2)_u$  levels at about 0.3 au, and the flat minima of the levels which originate from the  $2p_{3/2}$  united-atom levels at 0.06 au. The second minimum of the  $1(1/2)_u$  level has a depth of 50 eV. This interpretation allows us to predict the gross structure in the potential energy curve from even relatively crude correlation diagrams.

For the potential energy curves in figure 1 we calculated the classical elastic scattering cross sections  $d\sigma/d\Omega$  for centre-of-mass (CM) impact energies  $E_{CM}$  from 5 to 120 keV, and CM scattering angles  $\theta$  from 1 to  $10^\circ$ . In this range of variables a scaled plot, based on the similarity theory of Lindhard *et al* (1968), is useful. The cross sections are plotted relative to those for the original Lenz-Jensen potential according to Lenz (1932) and Jensen (1932), as a function of the dimensionless variable  $s = \varepsilon \sin(\theta/2)$ , where  $\varepsilon$  is the reduced CM impact energy  $\varepsilon = E_{CM}a/Z_1Z_2$ , with the screening length  $a = 0.8853(Z_1^{2/3} + Z_2^{2/3})^{-1/2}$  in atomic units, and the atomic numbers  $Z_1$  and  $Z_2$ . The difference between the average Lenz-Jensen potential  $V_{aLJ}$ , and the original  $V_{LJ}$  consists in a slightly different choice of expansion coefficients in the screening functions  $V_{aLJ}$  (see Loftager *et al* 1979).

The results of these calculations are presented for our case Ne-Ne in figure 3 together with the experimental  $Ne^+ - Ne$  data of Loftager *et al* (1980) as a function of  $s$ . The experimental data have a relative accuracy of better than 4%, which is thrice the size of the symbols for the various laboratory impact energies. The value of  $s$  can



**Figure 3.** Differential elastic scattering cross sections for Ne-Ne. Experimental Ne<sup>+</sup>-Ne (Loftager and Kristensen 1980): +, 15 keV; ∇, 25 keV; ×, 75 keV.

be correlated to the internuclear distance  $R_0$  of closest approach, which is given on the top of figure 3. The SCF curve fits the experimental data beautifully, while the 2DFS curve gives only a relatively rough description. Using the  $R_0$  scale in figure 3, the minima in the relative cross sections can be correlated to the minima of the relative potential. This indicates that the scattering cross section is very sensitive to the specific structure of the interatomic potential in the vicinity of the distance of closest approach. At first glance it is astonishing that the adiabatic ground-state potential for the neutral system gives such a good description for the measured Ne<sup>+</sup>-Ne system. The relative difference between a Ne-Ne and a Ne<sup>+</sup>-Ne system is just one electron in an outer  $m_j = (1/2)_u$  state. The contribution to the total energy of such an electron is given in first order by the energy difference between the  $4(1/2)_u$  and the  $4(1/2)_g$  or  $1(3/2)_g$  one-electron levels of the correlation diagram in figure 2. Asymptotically for  $R \geq 1.5$  au, the splitting between these two levels  $\Delta E$  is relatively well described by the formula  $\Delta E = C \exp(-R/a)$ , which was used by Jones *et al* (1966) to describe the splitting between  $\pi_g$  and  $\pi_u$  levels of the Ne<sup>+</sup>-Ne system. This is no longer true for smaller internuclear distances  $R$ , where the correlation diagram in figure 2 demonstrates that the  $4(1/2)_u$  level is lowered again by a few eV at internuclear distances  $R < 1$  au. Thus the contribution of the outer levels to the total energy is never larger than 10–20 eV. In the range of distances of closest approach  $R_0 = 0.2$ – $1.0$  au, which is of interest in this experiment; the inaccuracy, due to admixtures of excited potential energy curves, is only less than 10 eV. This statement is more or less independent of the system Ne-Ne or Ne<sup>+</sup>-Ne. It should be noted that the results for  $R_0 \leq 1.0$  au are fairly independent of  $\alpha_x$  in the range 0.7–1.0.

This demonstrates that the observed structure is a specific fingerprint of the quasi-molecular effects and its related structures in the potential energy curve during collision. Additionally, the very good agreement for all distances  $R_0 < 0.6$  au shows that the collision process is very adiabatic for the energies involved, and inelastic contributions—concerning only weakly bound states—are negligible. For  $R_0 > 0.6$  au both curves begin to disagree somewhat, and the experimental data show a small dependence

on the impact energy. The smallest impact energy of 15 keV is systematically nearer to our fully adiabatic curve than the 25 keV experimental points. Also the observed minimum shifts to somewhat larger  $R_0$  values for smaller impact energies. This clearly demonstrates non-adiabatic influences in the elastic cross sections.

In conclusion one may say that our adiabatic molecular calculations for the interatomic potential of the system Ne-Ne lead to a very good description of elastic ion-atom scattering. The detailed inner-shell interaction during collision can be understood in a quantitative way as a quasi-molecular effect. In the outer-shell region inelastic contributions begin to influence the scattering process. Thus the adiabatic quasi-molecular description—although still a guideline estimate—becomes inadequate. In view of our present results it is now possible to understand in detail the large amount of experimental data already existing.

The authors thank P Loftager for several discussions, and for making his unpublished results available.

## References

- Becke A D 1982 *J. Chem. Phys.* **76** 6037  
Dietz K and Weymans G J 1984a *J. Phys. B: At. Mol. Phys.* **17** 2987  
— 1984b *J. Phys. B: At. Mol. Phys.* **17** 4801  
Dunlap B I, Conolly J W D and Sabin J R 1979 *J. Chem. Phys.* **71** 4993  
Gärtner K and Hehl K 1979 *Phys. Stat. Solidi B* **94** 231  
Gombas R 1956 *Handbuch der Physik* vol 36 ed S Flügge (Berlin: Springer) p 109  
Hartung H and Fricke B 1983 *Phys. Scr.* **T 3** 244  
Hartung H, Fricke B, Lenz H and Sepp W-D 1982 *Phys. Lett.* **91A** 160  
Jensen H 1932 *Z. Phys.* **77** 722  
Jones P R, Eddy N W, Gilman H P, Ihaveri A K and Van Dyk G 1966 *Phys. Rev.* **147** 76  
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133  
Laaksonen L 1983 *Thesis* Dept of Physical Chemistry, Åbo Akademi, Finland  
Lenz W 1932 *Z. Phys.* **77** 713  
Lindhard J, Nielsen V and Scharff M 1968 *K. Danske Vidensk. Selsk. Mat.-Fys. Meddr.* **36** No 10  
Loftager P, Besenbacher F, Jensen O S and Sørensen V S 1979 *Phys. Rev. A* **20** 1443  
Loftager P and Kristensen P 1981 *Annual Report 1979/80, Institute of Physics, University of Aarhus, Denmark*  
p 33  
Nikulin V K 1971 *Zh. Tekh. Fiz.* **41** 41 (1971 *Sov. Phys.-Tech. Phys.* **16** 28)  
Schwarz K 1972 *Phys. Rev. B* **5** 2466  
Sepp W-D, Sengler W, Kolb D, Hartung H and Fricke B 1984 *Chem. Phys. Lett.* **109** 233  
Torrens I M 1972 *Interatomic potentials* (New York: Academic)  
Wilson W D and Bisson C L 1971 *Phys. Rev. B* **3** 3984