# Mobility and diffusion of atomic helium and neon ions in their parent gases

To cite this article: H R Skullerud and P -H Larsen 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 1017

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# Mobility and diffusion of atomic helium and neon ions in their parent gases

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**Abstract.** The mobility and the diffusion tensor have been calculated for $He^+$ ions in He and $Ne^+$ ions in Ne, at temperatures of 77–78 and 294 K, and at field-to-density values $E/n_0$ up to 2000 Td. For $He^+$ ions in He, *ab initio* potentials were used, with a careful extrapolation to large distances. A slight adjustment of the mean potential resulted in agreement between calculated mobilities and the best experimental values to better than 0.5%. For $Ne^+$ ions in Ne, a potential model with three adjustable parameters was constructed, and an overall agreement between measured and calculated mobilities to better than 1% was obtained. The model potentials probably give a good estimate of the gerade–ungerade splitting at internuclear distances from 7.5 to 10 au, but are not expected to be accurate at shorter distances .

## 1. Introduction

The motion of atomic noble gas ions in their parent gases and an electrostatic field has been the subject of a large number of both experimental and theoretical studies, over a time span of more than half a century (see e.g. Massey 1971).

The transport of charge in these atomic ion–parent gas systems is strongly influenced by resonant electron transfer processes, taking place at relatively large internuclear distances. Qualitatively, such electron transfer processes are equivalent to elastic collisions with nearly 180° deflection angle, and the angular distribution in the scattering therefore becomes strongly peaked in the forward and backward directions. This anisotropy in the scattering in turn gives rise to very anisotropic ionic velocity distribution functions, except at very weak fields.

Semiquantitatively, the ion transport processes have been well understood since Sena (1946) introduced his 'relay race method', applicable (with the correction of a minor error(Skullerud 1969)) to an idealised charge transfer model at strong fields. However, accurate calculations for realistic models at arbitrarily strong fields have remained a problem and, especially, no reliable calculations of strong-field transverse diffusion have been reported.

The scattering calculations demand accurate knowledge of the splitting between the gerade and ungerade potentials at relatively large distances, and these cannot be calculated with present day *ab initio* techniques. At very large distances, a method introduced by Holstein (1952), and extended by Bardsley *et al* (1975), can be used, if the asymptotic form of the atomic one-electron wavefunction is known. However, not even for a system as simple as $He^+$ in He is it admissible to extrapolate directly

from the asymptotic region to the 'ab initio region', and the construction of sufficiently accurate potential curves still is a problem.

For the He$^+$–He system, accurate *ab initio* potential curves for both the gerade and the ungerade potential have only very recently become available (Metropolous *et al* 1987). By combining these curves with the asymptotic theory of Bardsley *et al*, and using the known results for the H$_2^+$ molecular ions as a guide in bridging the gap, we have been able to construct potentials that could form a reasonable starting point for a transport calculation, and subsequently for a comparison between calculated and measured transport coefficients. This is reported in section 3.

For the Ne$^+$–Ne system, neither asymptotic electron wavefunctions nor reliable short- and intermediate-range *ab initio* potentials are available. We have nevertheless attempted a study also of this system, based upon potential models with three adjustable parameters. This is reported in section 4.

As a preliminary for the study of these two specific systems, a survey over the relevant scattering theory and the transport theory is given in section 2.

## 2. Theory

The calculation of transport coefficients proceeds in two steps. First a quantal or quasi-classical calculation of transport cross sections is performed, with the use of properly symmetrised adiabatic interaction potentials. The cross sections are subsequently used as input for a Galerkin-type solution of the Boltzmann equation.

The calculation of transport cross sections should in principle be quite straightforward. Some of the expressions found in the literature are however quite cumbersome. Also, there has been some confusion about the symmetry properties. We therefore present first a derivation of the cross section formulae used here, and then proceed to give details about the solution of the Boltzmann equation.

### 2.1. Potentials and symmetries

Naturally occurring helium and argon are nearly isotopically pure, while neon is a 10 : 1 mixture of two isotopes. In all these gases, most of the ion–parent gas atom collisions will be between particles with identical nuclei, and the nuclear spin is $I = 0$. We therefore concentrate on treating ion–atom collisions for identical and $I = 0$ nuclei systems.

All the noble gas atoms, except helium, have outer filled p shells. In a Born–Oppenheimer separation of electronic and nuclear motion, and with neglect of spin–orbit interaction, this gives rise to $\Sigma^+$ and $\Pi$ quasimolecular scattering states. In helium, only $\Sigma^+$ states form. The states $\Sigma_g^+$ and $\Sigma_u^+$ are symmetric and antisymmetric, respectively, on interchange of nuclei, while the doubly degenerate $\Pi$ states *a priori* have no specific nuclear interchange symmetry. By linear combinations of the degenerate states, one may however form two g–u potential pairs with opposite symmetries, $\Pi_{g,u}^+$ and $\Pi_{g,u}^-$ (Herzberg 1950). The molecular quantum number $\Lambda$ ($\Lambda = 0$ for $\Sigma$ states, 1 for $\Pi$ states, etc) has no direct connection with the nuclear interchange symmetry. Several earlier works give, nevertheless, cross section expressions implying a direct connection (Smith 1967, Heiche and Mason 1970, Viehland and Hesche 1986). These expressions are only correct for $\Sigma^+$ states, and must not be (and have apparently not been) applied to other states.

In a partial-wave expansion, with identical and spinless nuclei, even $l$ values couple to the symmetric states ($\Sigma_g^+$, $\Pi_g^+$, $\Pi_u^-$), and odd $l$ values to the antisymmetric ones. The cross sections are the averages of the cross sections for the distinct g–u pairs—and it is seen that nuclear symmetry requirements effectively only affect the $\Sigma$ states.

When spin–orbit interaction is taken into account, the above considerations have to be changed, in a way similar to the transition from Hund's cases a (for $\Pi$ states) and b (for $\Sigma$ states) to Hund's case c. The orbital and spin angular momenta are first coupled to give a resultant angular momentum $J$, with a projection $\Omega' = \pm\Omega$ along the internuclear axis. This gives rise to three doubly degenerate g–u potential pairs, $(J,\Omega) = (3/2, 3/2)$, $(3/2, 1/2)$ and $(1/2, 1/2)$; those with $J = 3/2$ describing the scattering of the ground state $^2P_{3/2}$ ion and the $(1/2, 1/2)$ pair describing the scattering of the metastable $^2P_{1/2}$ ion. As for the $\Lambda \neq 0$ states discussed above, the degenerate $\Omega \neq 0$ states can be combined to give states with specific and opposite nuclear interchange symmetries, $(J,\Omega) \rightarrow (J,\Omega)^+$, $(J,\Omega)^-$. This effectively means that nuclear symmetry requirements do not influence the calculated transport cross sections $\bar{\sigma} = (\sigma^+ + \sigma^-)/2$ for neon and the heavier noble gases.

The above considerations are valid only in an adiabatic approximation. For P-state ions, 'gyroscopic terms' will modify the centrifugal potential (see e.g. Geltman 1969). We have, however, not made any attempt to include this or other non-adiabatic effects in our analysis.

The spin–orbit interaction energy can, to a good approximation, be assumed not to vary significantly with the internuclear distance $R$, over the $R$ range of interest for the present problems. The spin–orbit mixed $(3/2, 1/2)$ and $(1/2, 1/2)$ potentials can then be found from the $(\Sigma, \Pi)$ potentials by solving the secular equation

$$\begin{vmatrix} E(\Pi) - \alpha - V & \sqrt{2}\alpha \\ \sqrt{2}\alpha & E(\Sigma) - V \end{vmatrix} = 0 \tag{1}$$

where

$$\alpha = (E(^2P_{3/2}) - E(^2P_{1/2}))/3$$

as outlined by Cohen and Schneider (1974). The $(3/2, 3/2)$ potentials are identical to the $\Pi$ potentials.

For one g–u pair, the interaction potentials are conveniently expressed through a mean potential $\bar{V}$ and a difference potential $\delta V$;

$$V_{g,u}(R) = \bar{V}(R) \pm \delta V(R)/2. \tag{2}$$

The mean potential can asymptotically be written as a dispersion–polarisation series

$$\bar{V}(R) \sim V_d(R) = -C_4/R^4 - C_6/R^6 \ldots . \tag{3}$$

In atomic units, $C_4 = \alpha^0/2$, where $\alpha^0$ is the atomic polarisability, while $C_6$ may be found approximately from the expression (see Mason and McDaniel 1988)

$$C_6 \approx \tfrac{3}{2}\alpha^0\alpha^+/(1/\epsilon^0 + 1/\epsilon^+) + \tfrac{1}{2}\alpha_q. \tag{4}$$

Here, $\alpha^+$ is the dipole polarisability of the ion, $\epsilon^0$ and $\epsilon^+$ the respective ionisation energies and $\alpha_q$ the quadrupole polarisability of the atom. For the systems considered in this paper, the $\alpha_q$ term is the most important in the expression for $C_6$.

The difference potential $\delta V(R)$ may, for $Ng^+$–$Ng$ systems and Russell–Saunders coupling, asymptotically be written in a form derived by Bardsley *et al* (1975);

$$\delta V(R) \sim (-1)^\Lambda \frac{2L+1}{4\Lambda!} \frac{(L+\Lambda)!}{(L-\Lambda)!} \left(\frac{v}{2R}\right)^\Lambda R u_0^2 \left(\frac{R}{2}\right) \left(\frac{4}{e}\right)^v$$

$$\times \left(1 + \frac{v}{2R}[v(3v-2) + \Lambda(2v-3\Lambda-3) - 2(L+\Lambda+1)(L-\Lambda)]\right) \tag{5}$$

where $v = 1/\sqrt{2\epsilon^0}$, $L = 0$ for helium and $L = 1$ for the other systems, $\Lambda = 0$ for $\Sigma$ states and $\Lambda = 1$ for $\Pi$ states, and $u_0(R/2)$ is the radial wavefunction for an outer-shell electron at the midplane between the two nuclei. Asymptotically, $u_0(r)$ may be written in the form

$$u_0(r) \sim A_v r^{v-1} e^{-r/v} \{1 + \tfrac{1}{2} v[L(L+1) - v(v-1)]/r\} \tag{6}$$

where $A_v$ is a normalisation factor, which cannot be obtained from an asymptotic analysis.

At intermediate and small internuclear distances, approximations to the interaction potentials can be found e.g. by Hartree–Fock or configuration interaction methods. These methods do not, however, usually give results that extrapolate accurately towards the asymptotic forms. This presents a problem for the calculation of the transport properties for the $Ng^+$–$Ng$ systems, where the range $R \sim 5$–12 au is of the utmost importance for the results.

## 2.2. Calculation of transport cross sections

The transport cross sections $\sigma_\lambda$ are defined as (see e.g. Kumar *et al* 1980)

$$\sigma_\lambda(g) = 2\pi \int (1 - P_\lambda(\cos\chi))\sigma_\Omega(g,\chi) \, d(\cos\chi) \tag{7}$$

where $g$ is the relative speed, $P_\lambda$ is a Legendre polynomial, $\chi$ the scattering angle and $\sigma_\Omega(g,\chi)$ the angular cross section.

In a partial wave representation, the angular cross section is given by the phaseshifts $\eta_l(k)$ as

$$\sigma_\Omega(g,\chi) = (4k^2)^{-1} \left| \sum_{l=0}^\infty (2l+1)(e^{2i\eta_l} - 1)P_l(\cos\chi) \right|^2 \tag{8}$$

where $k = m_r g/\hbar$ is the wavenumber.

Insertion of equation (8) into equation (7) yields an expression containing integrals over products of three Legendre polynomials. These integrals are readily evaluated using the expression (see Whittaker and Watson 1927)

$$P_m(x)P_n(x) = \sum_{r=0}^{\min(m,n)} \frac{B_{m-r}B_r B_{n-r}}{B_{n+m-r}} \frac{n+m-2r+1/2}{n+m-r-1/2} P_{n+m+2r}(x) \tag{9}$$

where the coefficients $B_m$ may be found from the recursion formula

$$B_m = \frac{2m-1}{2m} B_{m-1} \qquad \text{with } B_0 = 1. \tag{10}$$

After some straightforward algebra, one thus finds

$$\sigma_\lambda = \frac{4/\pi}{k^2} \sum_{l=0}^{\infty} \sum_{r=0}^{[(\lambda-1)/2]} C(l,\lambda,r) \sin^2(\eta_{l_1} - \eta_l) \tag{11}$$

where the quantities $C(l,\lambda,r)$ and $l_1$ are

$$C(l,\lambda,r) = \frac{(2l+1)(2l_1+1)}{l+l_1+\lambda+1} \frac{B_r B_{l-r} B_{\lambda-r}}{B_{l_1+r}} \tag{12}$$

$$l_1 = l + \lambda - 2r. \tag{13}$$

When applied to the calculation of scattering on one single g–u potential pair, with indistinguishable and spinless nuclei, the even-$l$ phaseshifts must be calculated from the potential curves corresponding to electronic states symmetric on nuclear interchange, and the odd-$l$ phaseshifts from the other potential,

$$\eta_{2k} = \eta_{2k}^{(s)} \qquad \text{and} \qquad \eta_{2k+1} = \eta_{2k+1}^{(a)}. \tag{14}$$

Apart from this, the cross section calculation is the same as for elastic scattering on a single potential curve.

At high energies (in the present context meaning of order 0.001 au or more), a large number of partial waves will contribute significantly to the sum in equation (11). The expression then approaches a 'quasiclassical limit', i.e. a limit where $l$ can be treated as a continuous variable, and the phaseshifts can be calculated by semiclassical methods and be related to the classical deflection angle $\Theta(b)$, $b$ being the impact parameter (see e.g. Child 1974)

$$l + 1/2 \to kb \tag{15}$$

$$2d\eta_l/dl \to \Theta(b). \tag{16}$$

To arrive at the quasiclassical expression for $\sigma_\lambda$, we substitute for $\eta_{l_1} \equiv \eta(l_1)$ a first-order series expansion around $l_1$, and take the high-$l$ limit of the expression for $C(l,\lambda,r)$;

$$\eta_{l_1} \approx \eta_l^{(l_1)} + (l_1 - l)\partial\eta_l^{(l_1)}/\partial l$$

$$\to \eta_l^{(l_1)} + \tfrac{1}{2}(\lambda - 2r)\Theta^{(l_1)}(b) \tag{17}$$

$$C(l,\lambda,r) \xrightarrow{l} (2l+1)B_r B_{\lambda-r}. \tag{18}$$

The superscript $l_1$ in (17) is inserted to keep track of the potential curve referred to. Using equations (13) and (14), this yields an expression

$$\sigma_\lambda = \pi k^{-2} \sum_l (2l+1) \sum_r 4B_r B_{\lambda-r} \sin^2[(\lambda-2r)\Theta^{(l)}(b)/2 + \Delta\eta(b)] \tag{19}$$

$$\Theta^{(l)}(b) = \begin{cases} \Theta^{(s)} & l = \text{even} \\ \Theta^{(a)} & l = \text{odd} \end{cases}$$

$$\Delta\eta(b) = \begin{cases} 0 & \lambda = \text{even} \\ \eta^{(s)}(b) - \eta^{(a)}(b) & \lambda = \text{odd}. \end{cases} \tag{20}$$

Using the identity (which is easily checked, but which we have not found referred to)

$$1 - P_\lambda(\cos\Theta) = \sum_{r=0}^{[(\lambda-1)/2]} 4B_r B_{\lambda-r} \sin^2[(\lambda - 2r)\Theta/2] \tag{21}$$

and replacing the sums over $l$ by integrals over $b$, we find after a little algebra the expressions

$$\sigma_{2\lambda} = \int d(\pi b^2)\{1 - \tfrac{1}{2}[P_{2\lambda}(\cos\Theta^{(s)}) + P_{2\lambda}(\cos\Theta^{(a)})]\} \tag{22}$$

$$\begin{aligned}
\sigma_{2\lambda+1} = \int d(\pi b^2)\bigg( &\{1 - \tfrac{1}{2}[P_{2\lambda+1}(\cos\Theta^{(s)}) + P_{2\lambda+1}(\cos\Theta^{(a)})]\}\cos^2(\eta^{(s)} - \eta^{(a)}) \\
&+ \{1 - \tfrac{1}{2}[P_{2\lambda+1}(\cos(\pi - \Theta^{(s)})) + P_{2\lambda+1}(\cos(\pi - \Theta^{(a)}))]\}\sin^2(\eta^{(s)} - \eta^{(a)}) \\
&+ \sum_{r=0}^{\lambda} B_r B_{2\lambda+1-r}\llbracket\sin\{[2(\lambda-r)+1]\Theta^{(s)} - \sin[2(\lambda-r)+1]\Theta^{(a)}\}\rrbracket \\
&\times \sin[2(\eta^{(s)} - \eta^{(a)})]\bigg). \tag{23}
\end{aligned}$$

In equation (23), the last term in the integrand oscillates rapidly at small $b$ values ($|\eta^{(s)} - \eta^{(a)}| \gg \pi$), and is small at large $b$ values ($|\Theta^{(s)} - \Theta^{(a)}| \ll \pi$). In the quasiclassical limit, it can therefore be neglected. Utilising the even parity of $P_{2\lambda}$, the expressions for $\sigma_{2\lambda}$ and $\sigma_{2\lambda+1}$ can then finally be merged into one formula,

$$\begin{aligned}
\sigma_\lambda = \int d(\pi b^2)\big( &[1 - \tfrac{1}{2}(P_\lambda(\cos\Theta^{(s)}) + P_\lambda(\cos\Theta^{(a)}))](1 - P_{ex}(b)) \\
&+ \{1 - \tfrac{1}{2}[P_\lambda(\cos(\pi - \Theta^{(s)})) + P_\lambda(\cos(\pi - \Theta^{(a)}))]\}P_{ex}(b)\big) \tag{24}
\end{aligned}$$

where $P_{ex}(b)$ is the semiclassical probability of charge exchange,

$$P_{ex}(b) = \sin^2(\eta^{(s)}(b) - \eta^{(a)}(b)). \tag{25}$$

Viehland and Hesche (1986) have derived quasiclassical expressions equivalent to equations (22) and (23), i.e. with a rapid oscillation term included. The expressions are not directly comparable to the present ones, as a different definition of the transport cross sections ($P_\lambda(\cos\chi) \to \cos^\lambda\chi$) was used. The expressions derived here (equations (24)–(25)) are in principle the same as used by Holstein (1952) and there is no need to use expressions more elaborate than these, when the energies are high enough to make a full quantal calculation unnecessary.

### 2.3. Calculation of transport coefficients

Our procedure for calculating the transport coefficients from a given set of transport cross sections is essentially as described by Larsen *et al* (1988). The only major difference is the choice of velocity space basis functions.

The equations to be solved are of form

$$\{\boldsymbol{a} \cdot \nabla_v + J\}f(\boldsymbol{v}) = h(\boldsymbol{v}) \tag{26}$$

where $\boldsymbol{a} = eE/m$ is the acceleration of an ion in the external electric field $\boldsymbol{E}$, and $J$ the Boltzmann collision operator. $h(\boldsymbol{v})$ is an inhomogeneous term having different forms for the equations governing the different transport coefficients.

Multiplication of equation (26) with polynomials $\Psi(\boldsymbol{v})$ and the insertion of a basis set expansion

$$f(\boldsymbol{v}) \to \sum_{j=1}^{N} \xi_j \phi_j(\boldsymbol{v}) \tag{27}$$

transforms equation (26) into a set of algebraic equations for the coefficients $\xi_j$.

The main problem in actually establishing these equations is the calculation of matrix elements of the collision operator:

$$J_{ij} = \int \Psi_i(\boldsymbol{v}) J(\phi_j(\boldsymbol{v})) \, \mathrm{d}\boldsymbol{v}. \tag{28}$$

Larsen *et al* (1988) showed how the $J_{ij}$ calculation can be reduced to the calculation of integrals of the form

$$J_j^{lmr} = \int \phi_j(\boldsymbol{v}) [\bar{v}_{lr}(v) v^{l+2r} Y_{lm}(\hat{v})] \, \mathrm{d}\boldsymbol{v} \tag{29}$$

where $\bar{v}_{lr}$ is a quantity with the dimension of a collision frequency, and $Y_{lm}$ is a spherical harmonic. They then proceeded to perform the quadrature for cases where the directional dependence of the basis functions $\phi_j(\boldsymbol{v})$ was also expressed through spherical harmonics.

In atomic ion–parent gas atom collisions, the scattering becomes progressively more peaked in the forward ($\chi \to 0$) and backward ($\chi \to \pi$) directions as the energy increases. This gives rise to very anisotropic ion velocity distributions at high field-to-density ratios $E/n_0$. An expansion of the directional dependence in spherical harmonics is then not very suitable.

We have chosen to use as basis sets Cartesian coordinate polynomial expansions around cylindrical coordinate weight functions

$$w(\boldsymbol{v}) = w_T(v_T^2) w_z(v_z) \tag{30}$$

where $v_z = \boldsymbol{v} \cdot \hat{\boldsymbol{a}}$ and $v_T^2 = v^2 - v_z^2$. For $w_z(v_z)$ we use a form approximating the convolution of a one-dimensional cold gas distribution (see e.g. Skullerud 1969) with a Maxwellian. A rather rough approximation to the convolution integral is sufficient to achieve reasonably fast convergence. For $w_T(v_T^2)$, we use for the sake of simplicity a Gaussian form,

$$w_T(v_T^2) \propto \exp(-\alpha_T v_T^2). \tag{31}$$

It would seem reasonable to select the parameter $\alpha_T$ close to the inverse of the expected mean square transverse velocity $\langle v_T^2 \rangle$. It turned out, however, that to obtain

convergence in the transverse diffusion calculation at high values of $E/n_0$, this choice had to be abandoned, and a more flexible basis set was constructed by the superposition of two sets with different $\alpha_T$. This is described in more detail in section 3.

With the type of basis sets described, the integrals $J_j^{lmr}$ (equation (29)) reduce to double integrals, over $\mathrm{d}v_T^2$ and $\mathrm{d}v_z$. For the $\mathrm{d}v_T^2$ integration we chose a 10-point Gauss–Laguerre quadrature, and for the $\mathrm{d}v_z$ integration an adaptive trapezoidal rule. The final solution of the equations for the expansion coefficients $\xi_j$ in equation (27) was performed using a standard Gauss-elimination-type routine.

## 3. The He⁺–He system

The mobility of He⁺ ions in He was measured by Tyndall and Powell (1930), and its zero-field value was calculated theoretically by Massey and Mohr (1934), with a result in fair agreement with the experimental value. A large number of investigations of the He⁺–He system has been performed since then, and reviews covering the early works have been presented by Smirnov (1967) and by Massey (1971).

The most accurate experimental mobilities available today are those reported by Helm (1976, 1977). The mobility was measured at 77 K for $9 \leq E/n_0 \leq 40$ Td, and at 294 K for $10 \leq E/n_0 \leq 1200$ Td, with claimed accuracies in the range 0.7 to 1.5%—and repeatabilities usually about 0.1% .

Accurate theoretical calculations of mobilities also for non-vanishing fields were reported by Sinha *et al* (1979). They used as a starting point the $\Sigma_u^+$ ground state potential curve calculated *ab initio* by Maas *et al* (1976), and combined it with the asymptotic expressions of Bardsley *et al* (1975) (equation (5) of the present paper) for the g–u splitting to find an estimate also of the $\Sigma_g^+$ potential. Transport cross sections were obtained from fully quantal phaseshift calculations, and used as input to the two-temperature transport theory described by Lin and Mason (1979). Convergence problems associated with the two-temperature theory restricted the useful $E/n_0$ range to below 100 Td. The calculated mobilities, both at 77 and at 294 K, were of order 1% below the experimental values of Helm, and this is slightly outside the combined experimental and calculational errors.

In 1987, Metropolous *et al* reported a new CI calculation of the $\Sigma_g^+$ potential curve, obtained using essentially the same basis set as used by Maas *et al* (1976) to find the $\Sigma_u^+$ curve. The calculation shows that the asymptotic expression of Bardsley *et al* overestimates the splitting, and thus explains qualitatively the 1% too small mobilities obtained by Sinha *et al* (1979).

Recently, experimental values of the transverse diffusion to mobility ratio $D_T/\mu$ have become available, at 294 K and for $15 \leq E/n_0 \leq 2000$ Td (Stefánsson *et al* 1988), and can be used for comparison with theoretical values.

We will here describe the calculation of transport coefficients for the He⁺–He system, using the best available *ab initio* potentials—with slight modifications and extrapolations—and the transport theory sketched in section 2. The findings from this relatively simple system can then hopefully also serve as guidelines for investigations of the heavier Ng⁺–Ng systems.

### 3.1. Basis sets and convergence problems

In our initial investigations, we first calculated a set of transport cross sections $\sigma_\lambda(g)$ from the potentials derived by Sinha *et al* (1979) at 60 energies per decade and

using equation (11). The phaseshifts were calculated by Numerov integration of the Schrödinger equation, as in the work of Sinha *et al.* The subsequent calculation of transport coefficients was carried out as described in section 2.3, with a velocity space basis set expansion around one single weight function $w(v) = w_z(v_z)w_T(v_T^2)$ (equations (30)–(31)).

The scheme using one single weight function worked well for $E/n_0$ values up to 200 Td. At higher values, however, the numerical convergence deteriorated progressively, and especially for quantities associated with the motion transverse to the electric field, i.e. $\langle v_T^2 \rangle$ and $D_T$. Thus, at 300 Td there was a maximum difference of more than 2% between the $D_T$ values found from the five highest approximations (moment equations up to order $l_{max} = 12$ were used), and at 2000 Td this difference had increased to more than 10% .

The reason for the convergence problems was suspected to be an unsuitable transverse weight function $w_T(v_T^2)$, i.e. one that could not by a short polynomial modification be brought into a form resembling reasonably well the actual transverse velocity distribution function $f_T(v_T^2)$. To investigate this suspicion further, we performed a computer simulation study of the system, at a few selected $E/n_0$ values in the range 100 to 2000 Td. The simulation program was essentially as described by Skullerud and Holmström (1985).
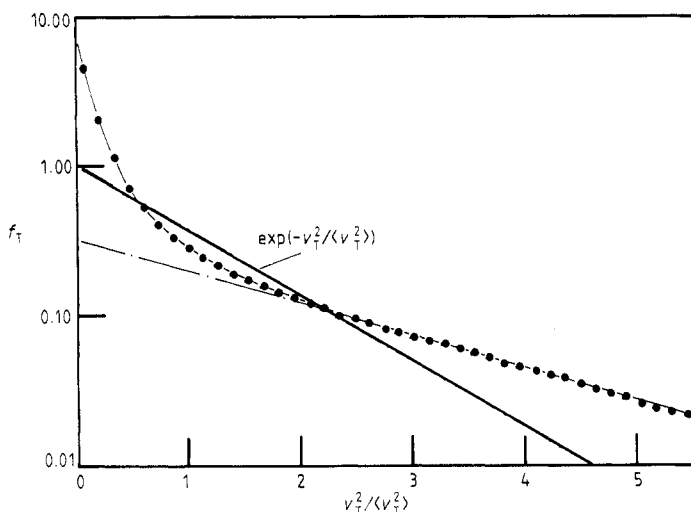


**Figure 1.** The transverse distribution function $f_T(v_T^2)$, for $He^+$ in He at 1200 Td and 295 K, from Monte Carlo simulation. For comparison, a Gaussian with the same variance is also shown.

Typical results of this study are shown in figure 1. The approximation $f_T(v_T^2) \propto \exp(-v_T^2/\langle v_T^2 \rangle)$ is clearly not very good, and becomes increasingly worse with increasing $E/n_0$. Qualitatively, one would rather regard $f_T(v_T^2)$ as composed of two components; one central and relatively narrow distribution $f_T^{(1)}(v_T^2)$ and a smaller but much more energetic distribution $f_T^{(2)}(v_T^2)$. Physically, the central peak can be depicted as originating from frequent, large impact parameter collisions, while the distribution $f_T^{(2)}$ originates from the much less frequent 'hard core collisions'.

In concordance with the simulation results, we changed the basis set expansion to

one utilising two different transverse weight functions,

$$f(\boldsymbol{v}) \rightarrow w_z(v_z) \left( w_T^{(1)}(v_T^2) \sum_{j_1} \xi_{j_1} P^{(j_1)}(\boldsymbol{v}) + w_T^{(2)}(v_T^2) \sum_{j_2} \xi_{j_2} P^{(j_2)}(\boldsymbol{v}) \right) \tag{32}$$

where $w_T^{(1)}$ and $w_T^{(2)}$ are Gaussians with different variances, and $P^{(j_1)}$ and $P^{(j_2)}$ are polynomial functions. After some trial and error with the variances, this turned out to be quite successful, and the apparent numerical convergence in the $D_T$ values improved by nearly a factor of 10 above 250 Td. This 'double Gaussian expansion' resembles the expansion used and discussed by Knierim *et al* (1981) in a study of hot atom reactions.

Above 2000 Td—where no experimental values are available—numerical convergence problems again became troublesome. We believe these problems are of a different nature to those appearing at lower values of $E/n_0$, mainly reflecting how the system of moment equations becomes increasingly ill-conditioned as the velocity distribution becomes narrower and the ratio $\langle v_T^2 \rangle / (\langle v_z^2 \rangle - v_{dr}^2)$ diminishes. Similar problems, in model calculations, have been reported by Waldman *et al* (1982). We have not found how to overcome these problems, and thus have to revert to Monte Carlo simulations if transport coefficients are wanted at very high values of $E/n_0$.

### 3.2. The interaction potentials

The *ab initio* interaction potentials of Maas *et al* (1976) and Metropolous *et al* (1987) are quite accurate for internuclear distances in the range 1–4 au. At larger distances, the absolute values of the potentials diminish rapidly, and the relative accuracies become progressively worse. Some method must thence be found to extrapolate to distances of order 8–12 au, in order to be able to perform the calculation of the transport cross sections.

The difference potential $\delta V(R)$ and the mean potential $\overline{V}(R)$ behave qualitatively differently at long distances, as seen from equations (3) and (5). We choose to represent them both relative to the values given by their asymptotic functional forms, and show them as functions of $1/R$;

$$\delta V_{rel} = \delta V / (A_v^2 e^{-v} R^{2v-1} e^{-R/v}) \tag{33}$$

$$\overline{V}_{rel} = \overline{V} / (-C_4 R^{-4}). \tag{34}$$

Consider first the function $\delta V_{rel}$ (figure 2). The quantity $v = 1/\sqrt{2\epsilon}$, where $\epsilon$ is the ionisation potential of the helium atom, while $A_v$ can be estimated from, e.g., the helium atom wavefunction calculations of Kinoshita (1957); $v = 0.7444$ and $A_v = 2.84$. These values are the same as were used by Bardsley *et al* (1975) and by Sinha *et al* (1979).

At small $1/R$ values, $\delta V_{rel}$ should approach the linear form (see equation (5))

$$\delta V_{rel} \sim 1 + v^2 (2 - v)/2R = 1 + 0.3479/R. \tag{35}$$

As a guide in the extrapolation of $\delta V_{rel}$ from the 'ab initio' regime' $1/R > 0.25$ to the asymptotic form, equation (35), we have in figure 2 also plotted the exact and the asymptotic forms of the relative splitting for the $H_2^+$ molecular ion, as obtained from Bates and Reid (1968) and Damburg and Propin (1968). The full curve in figure 2 shows our final choice. Some other forms were also tested, but it was found that only
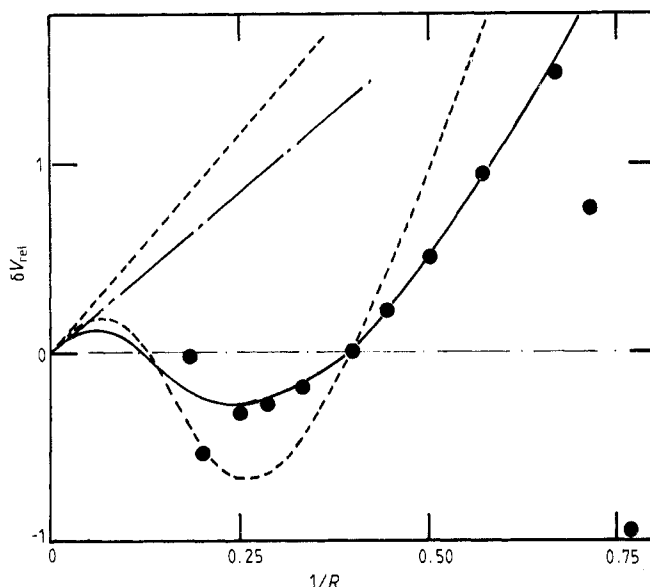
**Figure 2.** Relative $He_2^+$ potential splittings $\delta V_{rel}(1/R)$ (equation (33)). Circles, *ab initio* values; chain curve, asymptotic form (equation (35)); full curve, present choice. For comparison, the exact and asymptotic forms for the $H_2^+$ ion are also shown (broken curves).

slight modifications could be made in the region $1/R \in (0.1, 0.125)$ without affecting the mobility at strong fields too much.

The peculiar form of $\delta V_{rel}$ for $1/R > 0.6$ is due to avoided curve crossings on the $\Sigma_g^+$ potential. These do however occur at energies too high to influence the present transport calculations. To facilitate the representation of the potential, we have therefore chosen to use at larger $1/R$ values a 'diabatic splitting'.

Consider then the mean potential $\overline{V}$. This can be represented quite accurately by an analytical form, as suggested by Tang and Toennies (1984) for closed-shell systems,

$$\overline{V}(R) \approx Ae^{-BR} - \sum_{n=2}^{\infty} C_{2n}R^{-2n}f_{2n}(R) \tag{36}$$

$$f_{2n}(R) = 1 - \left( \sum_{k=0}^{2n} \frac{(BR)^k}{k!} \right)e^{-BR}. \tag{37}$$

Tang and Toennies used a constant value for $B$. Our experience from closed-shell configurations (Larsen *et al* 1988) has however shown that equation (37) may tend to cut off the dispersion series at somewhat too large $R$ values. To allow an adjustment for this, we introduce a modification

$$B \to B_1(R) = B(1 + R^2\delta). \tag{38}$$

The sum in equation (36) was truncated at $2n = 10$. The value of $C_4$ was taken from the tables of Teachout and Pack (1971), $C_6$ and $C_8$ were obtained from the variational calculations of Davison (1966), and $C_{10}$ (which is not very important) was estimated

as outlined by Ahlrichs *et al* (1988); $C_4 = 0.691\ 56$, $C_6 = 1.59$, $C_8 = 7.3$ and $C_{10} = 48$. $A$, $B$ and $\delta$ were first chosen to give an optimal fit to the *ab initio* potentials, and were then varied slightly to give an improved agreement between calculated and measured mobilities. The finally chosen values, used in plotting the function $\overline{V}_{rel}(1/R)$ in figure 3, were $A = 8.20$, $B = 2.065$ and $\delta = 0.004$.
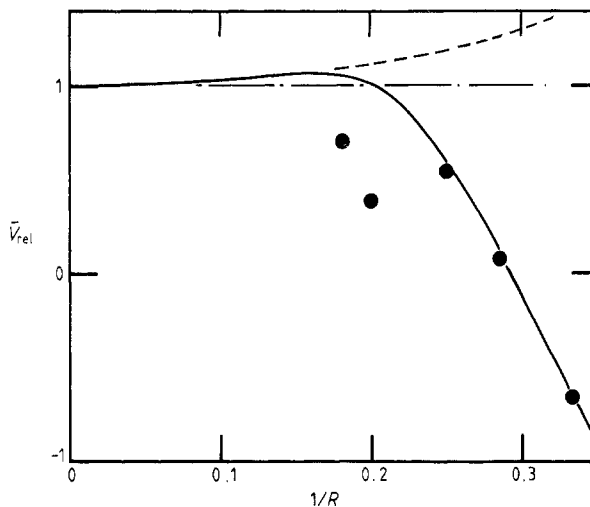


**Figure 3.** Relative $He_2^+$ mean potentials $\overline{V}_{rel}(1/R)$ (equation (34)). Circles, *ab initio* values; full curve, present choice; broken curve, the asymptotic form (equation (3)).

### 3.3. Calculated transport coefficients

The drift velocity $v_{dr}$ and the longitudinal and transverse diffusion coefficients $D_L$ and $D_T$ were calculated as functions of $E/n_0$ at 77 and 294 K.

At high values of $E/n_0$, only the difference potential $\delta V(R)$ has any noticeable influence on the value of the drift velocity, and this fact was used to tune $\delta V(R)$ to yield agreement with experiment. At low values of $E/n_0$, and especially at 77 K, also the mean potential is important, and variation of $\overline{V}(R)$ can change the calculated weak field mobilities by up to $\pm 2.5\%$ . This finding was used to tune $\overline{V}(R)$, i.e. the potential parameters $A$, $B$ and $\delta$, until acceptable agreement also with the weak field mobilities was also obtained.

The final potentials are listed in table 1, together with interpolated values of the *ab initio* potentials, and the calculated transport coefficients and mean ion energies are shown in table 2. Figure 4 shows a comparison between calculated and experimental mobilities, while the value of the product $n_0D_T$ is shown in figure 5.

In the calculations reported above, a fully quantal calculation of the transport cross sections was used. It may be of some interest to know whether the use of a quasiclassical calculation (equation (24)) might have been sufficient, as such a calculation is considerably faster. The calculations were therefore repeated with the use of quasiclassical cross sections. Figure 4 also shows how this changes the results, and indicates that fully quantal calculations should be used to obtain acceptable accuracies below 200 Td. We also tested two other variations of the cross section calculation; the use of the quasiclassical expression equation (23), where rapid oscillations are included,

**Table 1.** He$^+$–He potentials (MA76, Maas *et al* (1976); ME87, Metropolous *et al* (1987)).

| $R$ | $\Sigma_u^+$ | | $\Sigma_g^+$ | |
|---|---|---|---|---|
| | MA76 | Present | ME87 | Present |
| 1.3 | 0.0548 | 0.0447 | 0.7420 | (0.970) |
| 1.4 | 0.0057 | −0.0016 | 0.7477 | (0.814) |
| 1.5 | −0.0296 | −0.0349 | 0.6860 | (0.684) |
| 1.75 | −0.0771 | −0.0796 | 0.4485 | 0.4462 |
| 2.0 | −0.0902 | −0.0911 | 0.2947 | 0.2941 |
| 2.25 | −0.0867 | −0.0872 | 0.1966 | 0.1964 |
| 2.5 | −0.0763 | −0.0764 | 0.1328 | 0.1327 |
| 3.0 | −0.0515 | −0.0518 | 0.0628 | 0.0629 |
| 3.5 | −0.0315 | −0.0319 | 0.0309 | 0.0308 |
| 4.0 | −0.018 336 | −0.018 65 | 0.0155 | 0.01534 |
| 4.5 | | −0.010 70 | | 0.00772 |
| 5.0 | −0.005 84 | −0.006 07 | 0.0038 | 0.003 85 |
| 5.5 | −0.003 24 | −0.003 46 | 0.0022 | 0.001 876 |
| 6.0 | | $-1.995\times10^{-3}$ | 0.0010 | $8.64\times10^{-4}$ |
| 6.5 | | $-1.173\times10^{-3}$ | | $3.53\times10^{-4}$ |
| 7.0 | | $-7.08\times10^{-4}$ | 0.0004 | $1.027\times10^{-4}$ |
| 7.5 | −0.000 33 | $-4.43\times10^{-4}$ | | $-1.35\times10^{-5}$ |
| 8.0 | | $-2.89\times10^{-4}$ | 0.0002 | $-6.18\times10^{-5}$ |
| 9.0 | | $-1.402\times10^{-4}$ | | $-7.71\times10^{-5}$ |
| 10.0 | −0.000 04 | $-7.96\times10^{-5}$ | −0.0001 | $-6.21\times10^{-5}$ |
| 11.0 | | $-5.06\times10^{-5}$ | | $-4.58\times10^{-5}$ |
| 12.0 | | $-3.46\times10^{-5}$ | | $-3.33\times10^{-5}$ |
| $V_{min}$ | −0.090 38 | −0.0913 | | |
| $R_{min}$ | 2.063 | 2.039 | | |

and the use of the quantal expression equation (11), but with semiclassically calculated phaseshifts. No noticeable improvement was found compared with the results obtained using the simplest quasiclassical expression, equation (24).

### 3.4. Discussion

A comparison between the *ab initio* $\Sigma_u^+$ potential and the present mobility-modified one shows the latter to be slightly shifted towards smaller $R$ values, in the region around and inside the minimum. Also, the minimum is slightly deeper. The shifts are qualitatively in agreement with the presumably very accurate calculation of the position of the minimum by Liu (1971), who found a position $R_{min} = 2.044$—to be compared with the value 2.0625 used by Maas *et al* (1976).

Maas *et al* (1976) adjusted their *ab initio* $\Sigma_u^+$ potential to yield agreement with translational spectroscopy measurements on predissociative He$_2^+$ ions. The adjustment was performed using a least squares method, and resulted, effectively, in a lowering of the potential curve by about 0.006 au for all values of $R$, but without any shift in the position. It seems to us as if this adjustment must be too large at the largest $R$ values, giving potential values not compatible with the known asymptotic behaviour. This may have been compensated for by too small adjustments at small $R$ values. However, perhaps the most essential thing to learn from a comparison between the present 'mobility-modified potential' and their 'translational spectroscopy modified potential' is that neither of these modifications can be claimed to be unique in any way.

**Table 2.** Calculated mobilities, mean energies and diffusion to mobility ratios for $He^+$ ions in helium, at 77 and 294 K.

| $E/n_0$ (Td) | $n_0\mu$ (m Td$^{-1}$ s$^{-1}$) | $\frac{1}{2}m\langle v^2 \rangle$ (meV) | $D_L/\mu$ (mV) | $D_T/\mu$ (mV) | $T$ (K) |
|---|---|---|---|---|---|
| 1 | 43.76 | 10.03 | — | — | 77 |
| 2 | 43.54 | 10.27 | — | — | 77 |
| 5 | 42.20 | 11.81 | — | — | 77 |
| 10 | 39.41 | 16.24 | — | — | 77 |
| 15 | 36.85 | 22.06 | — | — | 77 |
| 20 | 34.70 | 28.76 | — | — | 77 |
| 24 | 33.23 | 34.57 | — | — | 77 |
| 32 | 30.78 | 47.04 | — | — | 77 |
| 40 | 28.85 | 60.34 | — | — | 77 |
| 1 | 28.42 | 38.04 | 25.35 | 25.34 | 294 |
| 2 | 28.41 | 38.14 | 25.39 | 25.35 | 294 |
| 5 | 28.28 | 38.85 | 25.70 | 25.50 | 294 |
| 10 | 27.92 | 41.27 | 26.69 | 25.92 | 294 |
| 15 | 27.40 | 45.03 | 28.15 | 26.53 | 294 |
| 20 | 26.81 | 49.82 | 29.92 | 27.30 | 294 |
| 40 | 24.41 | 75.82 | 35.58 | 31.11 | 294 |
| 60 | 22.40 | 108.0 | 48.2 | 35.40 | 294 |
| 80 | 20.79 | 143.5 | 58.1 | 39.8 | 294 |
| 100 | 19.47 | 180.9 | 68.4 | 44.2 | 294 |
| 150 | 17.05 | 279.9 | 95.1 | 55.0 | 294 |
| 200 | 15.38 | 384.1 | 123.4 | 65.5 | 294 |
| 400 | 11.77 | 831 | 247.3 | 104.9 | 294 |
| 600 | 9.97 | 1307 | 384 | 138.7 | 294 |
| 800 | 8.85 | 1803 | 532 | 167 | 294 |
| 1000 | 8.06 | 2312 | 689 | 192 | 294 |
| 1500 | 6.79 | 3644 | 1114 | 240 | 294 |
| 2000 | 6.01 | 5034 | 1568 | 278 | 294 |

The g–u splitting $\delta V(R)$ is shown in figure 2, relative to the asymptotic functional form. It is clear from the figure that the asymptotic correction, linear in $1/R$, found by Bardsley *et al* (1975), is applicable only at very large internuclear distances. In the region most important for the transport properties, it is in fact better to use the simple asymptotic form, without any $1/R$ correction term. This may possibly also be so for the other noble gas systems.

The comparison between calculated and experimental mobility values (figure 4) shows an agreement well within the combined uncertainties. It is possible to improve the agreement between the 77 K values somewhat, but with the claimed experimental accuracies this seems not to be worthwhile. A comparison between calculated and experimental transverse diffusion coefficients (figure 5), on the other hand, reveals an increasing discrepancy in the region above 500 Td. The reason for this discrepancy is not clear. An improved agreement can be obtained by adjusting the repulsive $\Sigma_g^+$ potential curve downwards for internuclear distances in the range 2.5 to 4 au, but the adjustments needed are larger than we find reasonable. A check of the accuracy of our calculations in the high $E/n_0$ region was performed by comparison with extended Monte Carlo calculations, but this revealed no error; the $D_T$ values obtained agreed within 1.5% at 2000 Td. There remains the possibility of some unnoticed error in the scattering calculations, or in the high $E/n_0$ measurements.
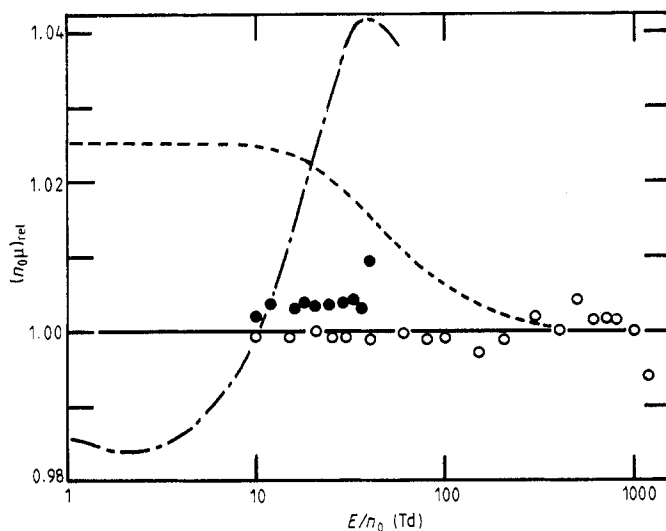
**Figure 4.** $He^+$–He reduced mobilities $n_0\mu$, relative to calculated values (table 2). Full circles, 77 K values of Helm (1976); open circles, 294 K values of Helm and Elford (1977); broken curve/chain curve, 294 K and 77 K values, respectively, calculated using quasiclassical theory.
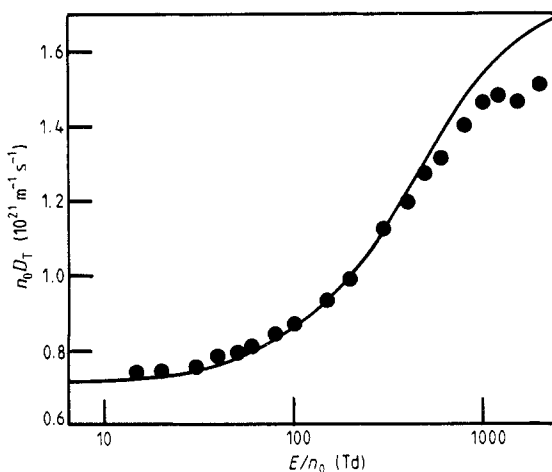


**Figure 5.** $He^+$–He reduced transverse diffusion coefficient $n_0 D_T$, at 294 K. Circles, experimental values of Stefánsson *et al* (1988); full curve, calculated values (table 2). The experimental $D_T/\mu$ values were converted to $n_0 D_T$ values using our calculated $n_0\mu$ values.

Waldman *et al* (1982) investigated the applicability of generalised Nernst–Townsend relations (relations between diffusion and mobility) on cases involving resonant charge transfer, using various models and also the calculations of Sinha *et al* for the $He^+$–He system. Viehland and Hesche (1986) have criticised the work, and claim—based on a comparison with the experimental results of Sejkora *et al* (1983)—that the $D_T/\mu$ values estimated by Waldman *et al* for the Sinha *et al* $He^+$–He model are inaccurate, due to an inadequate procedure for estimating the viscosity cross section $\sigma_2$. To

check these claims, we have calculated transport coefficients also for this model, with fully quantal cross sections. Table 3 shows a comparison between the three sets of results. Clearly, the estimates of Waldman *et al* are in very good agreement with our calculated values, while those of Viehland and Hesche are less accurate. The claims by Viehland and Hesche are thus not supported by the present findings. The apparent disagreement between our findings and those of Viehland and Hesche may be attributed to several causes. Firstly, we feel that they overestimated the expected accuracy of the generalised Nerst–Townsend relation. In our judgement, the difference between the values calculated by Waldman *et al* and those found by Viehland and Hesche is smaller than the expected accuracy of the expressions, and thus not significant. Secondly, they seem to have overestimated the accuracy of the experimental results of Sejkora *et al*, which have relatively large statistical errors, and probably also are distorted by systematic errors, as discussed by Stefánsson *et al* (1988). Thirdly, the model potential pair of Sinha *et al* yields mobilities about 1% too low, and thus should be expected to gives values of $(D_T/\mu - kT/e)$ in error by of order 2–3%, i.e. of the same order of magnitude as the differences discussed.

**Table 3.** $D_T/\mu$ values calculated using the potentials of Sinha *et al* (294 K). WMV, Waldman *et al* (1982); VH, Viehland and Hesche (1986).

| $E/n_0$ (Td) | $D_T/\mu$ (meV) | | |
|---|---|---|---|
| | WMV | VH | Present |
| 48.1 | 32.4 | 33.27 | 32.73 |
| 55.5 | 33.9 | 35.01 | 34.30 |
| 62.7 | 35.4 | 36.74 | 35.84 |
| 69.7 | 37.0 | 38.50 | 37.34 |
| 76.6 | 38.6 | 40.23 | 38.83 |
| 83.3 | 40.3 | 41.96 | 40.24 |

Viehland and Hesche (1986) also report that they have calculated transport coefficients for the He$^+$–He systems at 294 K and up to high values of $E/n_0$, with high accuracies and without convergence problems, using the potential of Sinha *et al*, but they do not give any numerical values. (Their values in table 3 were calculated using a generalised Nernst–Townsend relation, and not by solving the Boltzmann equation.) They do however report a difference of 20% between the $D_L$ values obtained in the two highest approximations at 300 Td, and 8% between the corresponding $D_T$ values. This may be an indication of similar convergence problems as those discussed in section 3.1.

## 4. The Ne$^+$–Ne system

In all the noble gases except helium, the spin–orbit coupling gives rise to a ground state $^2P_{3/2}$ ion and a metastable $^2P_{1/2}$ ion with slightly higher energy. In neon, the energy difference is 0.003 57 au

The mobilities of the two ions are generally quite close to each other, and the difference is not easily measured. However, Helm and Elford (1977) reported high resolution experiments at liquid nitrogen temperature, with two distinct mobility peaks observed at $E/n_0$ values below 30 Td. The two ions were found in relative abundances close to the ratio 2 : 1 between their statistical weights. The mobility difference

decreased with increasing $E/n_0$, and could not be resolved above 30 Td, nor in room temperature experiments.

Cohen and Schneider (1974) calculated the $Ne^+$–Ne potentials *ab initio*, using a valence bond CI method, and in a subsequent paper (Cohen and Schneider 1975) used the potentials to find the zero-field mobilities of the ions, as functions of the temperature. Qualitatively, the measured mobilities of Helm and Elford (1977) agreed with the predictions of Cohen and Schneider, but the calculated mobilities were of order 15% lower than the experimental ones.

Viehland and Hesche (1986) calculated the mobilities of the two $Ne^+$ ions at $E/n_0$ values from 0 to 320 Td and at temperatures of 78, 216 and 298 K, using as input to the calculations the potentials of Cohen and Schneider. However, the calculated mobilities were now found to be of order 20% *higher* than the experimental ones. The disagreement with the values obtained by Cohen and Schneider for presumably the same potentials is much too large to be accounted for by approximations in the transport calculations.

In addition to the experimental mobilities of Helm and Elford (1977), room temperature mobilities accurate to better than 1% have been reported by Hegerberg *et al* (1982), at $E/n_0$ values up to 1000 Td. Recently, also transverse diffusion measurements have been reported (Stefánsson 1989), at room temperature and for $E/n_0$ up to 2000 Td.

The agreement between theoreticallly predicted and experimentally observed mobilities is presently far from satisfactory. We will try to contribute to an understanding of the causes for the discrepancies, and further indicate how potentials may be constructed to yield transport coefficients in fair agreement with those observed experimentally.


### 4.1. Interaction potentials

Several attempts have been made at estimating the $Ne^+$–Ne interaction potentials theoretically. Generally, a Russell–Saunders coupling scheme has been used, with the spin–orbit splitting included semiempirically (see equation (1)).

The various results are not in very good agreement with each other, as reflected, e.g., in the values obtained for the dissociation energy $D_e$ of the ground state $(\frac{1}{2})_u(^2P_{3/2})$ molecular ion. Thus Gilbert and Wahl (1971) in an SCF calculation found $D_e = 0.061$ au, Cohen and Scneider (1974) in their valence bond CI calculation found $D_e = 0.043$ au, and Michels *et al* (1978) in a 'density functional' calculation found $D_e = 0.048$ au. Values as low as 0.02 au have been reported in earlier studies (see Mulliken 1970 for a review). An experimental estimate, from spectroscopic measurements on a neon afterglow (Connor and Biondi 1965, Frommhold and Biondi 1969) has given a value $D_e = (0.050 \pm 0.003)$ au.

Asymptotically, the mean potential $\bar{V}(R)$ should approach the values given by equation (3), with $C_4 = 1.332$ and $C_6 = 6.53$, and the splittings $\delta V^\Sigma$ and $\delta V^\Pi$ should approach the values given by equations (5) and (6). The normalisation constant $A_v$ in the expression for the asymptotic wavefunction $u_0(r)$ is however, in contrast to the helium case, not well known. The Hartree–Fock calculations of Froese Fischer (1972) yield a wavefunction asymptotically of the form given by equation (6), with $A_v = 1.92$, but with too small a value of $v$; 0.7668 instead of 0.7932. The difference in $v$ values reflects a well known shortcoming of the Hartree–Fock method, and also serves to indicate the approximate accuracy of the Hartree–Fock value of $A_v$.

Apart from the normalisation, the asymptotic forms of the splittings are known. For illustrative purposes, we have chosen a reference normalisation constant $A_{v0} = 1.90$,

and show in figure 6 the relative splittings

$$\delta V_{\text{rel}}^{\Sigma} = \delta V^{\Sigma}/(3A_{v0}^2 e^{-v} R^{2v-1} e^{-R/v}) \tag{39}$$

$$\delta V_{\text{rel}}^{\Pi} = \delta V^{\Pi}/(3v A_{v0}^2 e^{-v} R^{2v-2} e^{-R/v}) \tag{40}$$

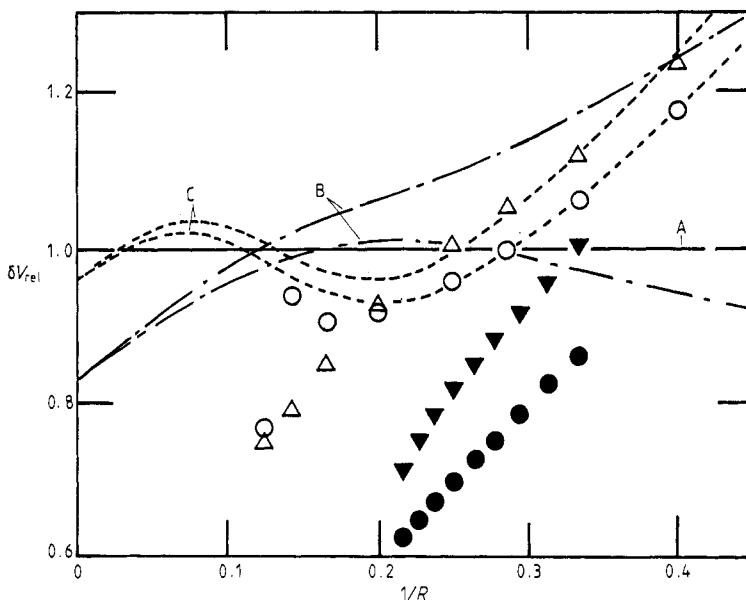as functions of $1/R$, as obtained from various calculations, and also some forms used as models in the present work.



**Figure 6.** Relative $\text{Ne}_2^+$ potential splittings $\delta V_{\text{rel}}(1/R)$ (equations (39)–(40)). Open triangles/circles, $\Sigma$- and $\Pi$-state values, respectively, of Cohen and Schneider (1975); full triangles/circles, $\Sigma$- and $\Pi$-state values of Hobbs and Wright (1978); A, reference potential ($A_v = 1.90$); B, best fit $\Sigma$- and $\Pi$-state values based upon asymptotic theory with exponential extrapolation; C, attempt to join Cohen and Schneider's values with asymptotic theory behaviour.

Figure 7 shows mean potentials $\overline{V} = (V_{\text{g}} + V_{\text{u}})/2$, relative to the polarisation potential. Also shown is the known asymptotic form $(1 + (C_6/C_4)/R^2)$.

It is clear from figures 6 and 7 that the theoretically calculated interaction potentials do not give much guidance for a reasonable modelling of the real interaction potentials at internuclear distances $R$ larger than about 4 $a_0$. At smaller distances, one might try e.g. to fit to the *ab initio* potentials of Cohen and Schneider, but we have instead chosen to use various simple empirical forms for all values of $R$.

### 4.2. Transport calculations

Transport coefficient calculations were performed with a number of different trial potentials, all with three adjustable parameters.

The mean potential was chosen to have the form given by equations (36)–(37), with the sum truncated at $2n = 6$, and without the modification equation (38),

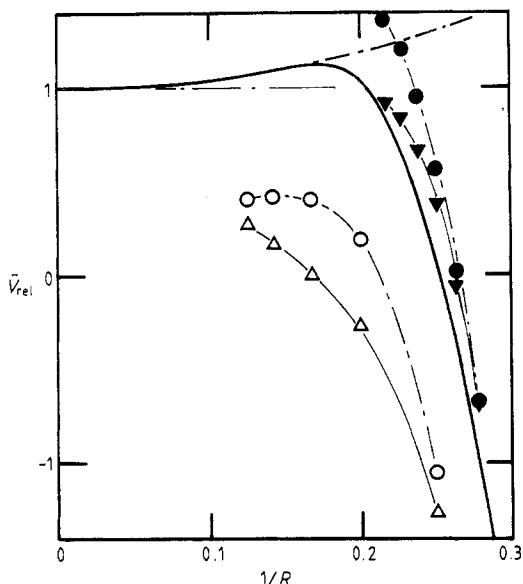$$\overline{V}(R) = A e^{-BR} - C_4 R^{-4} f_4(BR) - C_6 R^{-6} f_6(BR). \tag{41}$$

**Figure 7.** Relative $Ne_2^+$ mean potentials $\overline{V}_{rel}(1/R)$ (equation (34)). Open triangles/circles, $\Sigma$ and $\Pi$ values, respectively, of Cohen and Schneider (1975); full triangles/circles, $\Sigma$ and $\Pi$ values of Hobbs and Wright (1978); full curve, present choice; broken curve, the asymptotic form (equation (3)).

For the sake of simplicity, the same $\overline{V}(R)$ was used for the $\Sigma$ states and the $\Pi$ states.

For the potential splittings, various functional forms were tried. For all these forms, the relative splitting could be written as the product of a shape function $F(1/R)$ and a magnitude factor $M = (A_v/A_{v0})^2$.

$$\delta V_{rel} = MF(1/R) = (A_v/A_{v0})^2 F(1/R) \tag{42}$$

with $F(1/R \rightarrow 0) = 1.0$. The functions $F$ could be chosen differently for the $\Sigma$ states and the $\Pi$ states.

With chosen shape function $F$, a best fit to the experimental mobilities was obtained in two steps. First, some initial choice of the mean potential parameters $A$ and $B$ was made, and the magnitude factor $M$ was varied until the calculated high $E/n_0$ mobilities (294 K, 800–1000 Td) agreed with the experimental ones. Then, the parameters $A$ and $B$ were varied systematically until reasonable agreement was obtained between the calculated and experimental mobilities for the two fine-structure states of the ion, at 78 K and $E/n_0 \sim 10$–25 Td. The high-field mobilities were largely insensitive to the variation of the mean potential parameters.

Our simpest model (curve A in figure 6) used the asymptotic form of the splitting for all $R$ values, i.e. $F^{\Sigma} = F^{\Pi} = 1.0$. Going through the procedure described above, and using quasiclassically calculated cross sections, this gave a best value of the neon atomic electron wavefunction parameter $A_v = 1.90$. This value was subsequently used as a reference value ($A_{v0} = 1.90$). The corresponding best values of the mean potential parameters were $A = 65.5$ and $B = 2.28$.

To check the applicability of the quasiclassical method, we then performed a fully quantal scattering calculation, with the same potential parameters, and recalculated the transport coefficients. At 78 K, the maximum deviation between the two sets of

calculated mobilities was just below 0.3%, and at 294 K it was below 0.1%. Quasi-classical cross section calculations were therefore deemed to be sufficiently accurate for the remainder of the work.

Several other forms of the relative splitting were then tested. Some of these are shown in figure 6. Curves B are based upon the expressions of Bardsley *et al* (equations (5)–(6)), with a pure exponential extrapolation $(a\,e^{-bR})$ for $R < 5.0$), while curves C represent an attempt to fit together Cohen and Schneider's potential with an $H_2^+$-like asymptotic behaviour.

A main outcome of these exercises was that all the forms shown gave fits to the high $E/n_0$ experimental mobility values well inside the stated experimental accuracies, provided the magnitude factor $M$ was adjusted to yield $\delta V_{rel} \approx 1.00$ in the region $0.1 < 1/R < 0.125$.

These forms also admitted similarly good fits to the 77–78 K fine-structure resolved mobilities, when the mean potential parameters $A$ and $B$ were adjusted optimally. There was, however, a variation of up to $\pm 1.5\%$ in the mobilities found at 294 K and low to intermediate $E/n_0$ values. The potential C thus gave results 1.5% below the experimental values for $E/n_0 < 25$ Td, and was discarded.
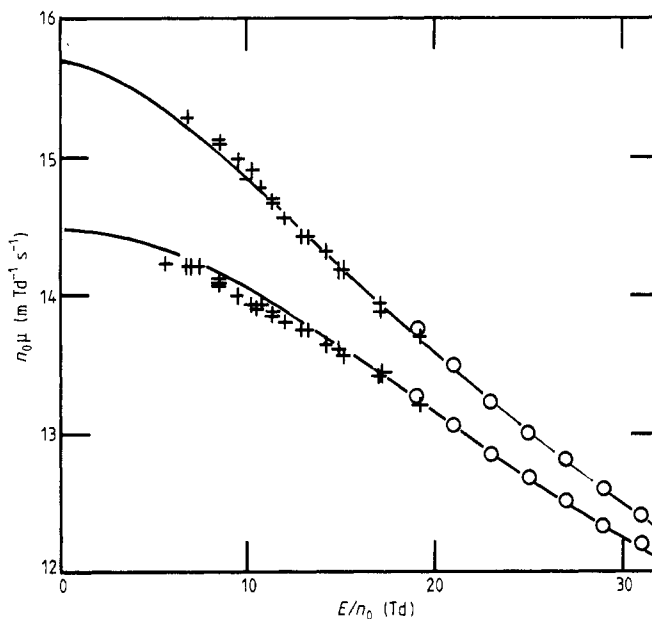


**Figure 8.** Reduced mobilities $n_0\mu$ for the two fine-structure states of the $Ne^+$ ion. Upper curve, calculated $^2P_{3/2}$ values (78 K); lower curve, calculated $^2P_{1/2}$ values (78 K); crosses/circles, experimental values of Helm and Elford (1977) at 77 and 78 K, respectively. (The mobility reduced to NTP, $\mathscr{K}_0$ $(cm^2\ V^{-1}\ s^{-1}) = (n_0\mu\ (m\ Td^{-1}\ s^{-1}))/2.6868$.)

In figure 8, we show a comparison between experimental mobilities and 78 K mobilities calculated from potential A. The other potentials gave nearly the same curves as those shown.

In figure 9, experimental and calculated room temperature mobilities are compared. The values obtained using potential A are arbitrarily chosen as a reference. Since the difference between the room temperature mobility values for the two spin states could
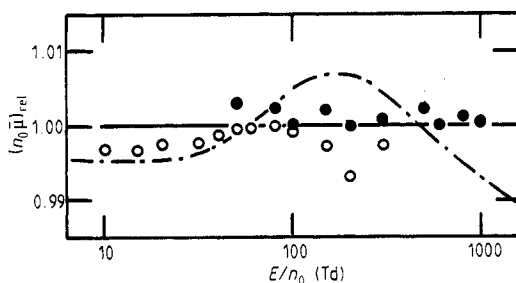
**Figure 9.** Ne$^+$–Ne state-averaged 294 K reduced mobilities $n_0\mu$ relative to the values obtained using potential A (table 4). Full circles, Hegerberg *et al* (1982); open circles, Helm and Elford (1977); chain curve, calculated from potential B.

**Table 4.** Calculated mobilities, mean energies and diffusion to mobility ratios for Ne$^+$ ions in neon, at 78 and 294 K. The table shows spin state averaged quantities ($\frac{2}{3}(^2P_{3/2}) + \frac{1}{3}(^2P_{1/2})$) and the relative (($^2P_{3/2}) - (^2P_{1/2})$) splittings as a percentage of the spin state averaged values.

| $E/n_0$ (Td) | $n_0\mu$ (m Td$^{-1}$ s$^{-1}$) | $\Delta n_0\mu$ (%) | $\frac{1}{2}m\langle v^2\rangle$ (meV) | $\overline{D_L/\mu}$ (mV) | $\Delta D_L/\mu$ (%) | $\overline{D_T/\mu}$ (mV) | $\Delta D_T/\mu$ (%) | $T$ (K) |
|---|---|---|---|---|---|---|---|---|
| 1 | 15.27 | 7.7 | 10.13 | — | — | — | — | 77 |
| 2 | 15.24 | 7.6 | 10.28 | — | — | — | — | 77 |
| 5 | 15.06 | 6.8 | 11.27 | — | — | — | — | 77 |
| 10 | 14.59 | 5.2 | 14.47 | — | — | — | — | 77 |
| 15 | 14.03 | 4.0 | 19.08 | — | — | — | — | 77 |
| 20 | 13.47 | 3.2 | 24.60 | — | — | — | — | 77 |
| 25 | 12.93 | 2.8 | 30.73 | — | — | — | — | 77 |
| 30 | 12.43 | 2.4 | 37.25 | — | — | — | — | 77 |
| 1 | 11.08 | 2.3 | 38.03 | 25.34 | 0.0 | 25.34 | 0.0 | 294 |
| 2 | 11.08 | 2.4 | 38.10 | 25.38 | 0.0 | 25.35 | 0.0 | 294 |
| 5 | 11.04 | 2.4 | 38.65 | 25.63 | 0.0 | 25.44 | 0.0 | 294 |
| 10 | 10.93 | 2.3 | 40.53 | 26.43 | 0.1 | 25.74 | 0.1 | 294 |
| 15 | 10.76 | 2.2 | 43.47 | 27.62 | 0.1 | 26.20 | 0.2 | 294 |
| 20 | 10.55 | 2.0 | 47.26 | 29.08 | 0.1 | 26.77 | 0.3 | 294 |
| 40 | 9.68 | 1.6 | 68.05 | 36.19 | −0.5 | 29.50 | 1.0 | 294 |
| 60 | 8.91 | 1.2 | 93.90 | 44.28 | −1.1 | 32.45 | 1.8 | 294 |
| 80 | 8.29 | 1.0 | 122.5 | 52.90 | −1.4 | 35.39 | 2.2 | 294 |
| 100 | 7.78 | 0.8 | 152.7 | 61.9 | −1.5 | 38.26 | 2.5 | 294 |
| 150 | 6.84 | 0.5 | 233.6 | 85.9 | −1.1 | 45.1 | 2.4 | 294 |
| 200 | 6.19 | 0.4 | 319.4 | 111.4 | −0.6 | 51.8 | 1.5 | 294 |
| 400 | 4.775 | 0.2 | 693.2 | 224.4 | −0.9 | 77.5 | −2.6 | 294 |
| 600 | 4.067 | −0.1 | 1098 | 348.4 | −2.6 | 102.1 | −6.4 | 294 |
| 800 | 3.620 | −0.4 | 1524 | 479 | −3.5 | 125.5 | −9.7 | 294 |
| 1000 | 3.303 | −0.6 | 1965 | 616 | −3.2 | 149 | −14 | 294 |
| 1200 | 3.064 | −0.9 | 2417 | 753 | −2.7 | 173 | −16 | 294 |
| 1500 | 2.790 | −0.7 | 3116 | 972 | −1.8 | 207 | −23 | 294 |

not be resolved, we have assumed that an averaged value $\frac{2}{3}\mu(^2P_{3/2}) + \frac{1}{3}\mu(^2P_{1/2})$ could be used for this comparison.

Finally, we show in figure 10 a comparison between transverse diffusion coefficients calculated from potential A, and experimental values obtained by Stefánsson (1989)
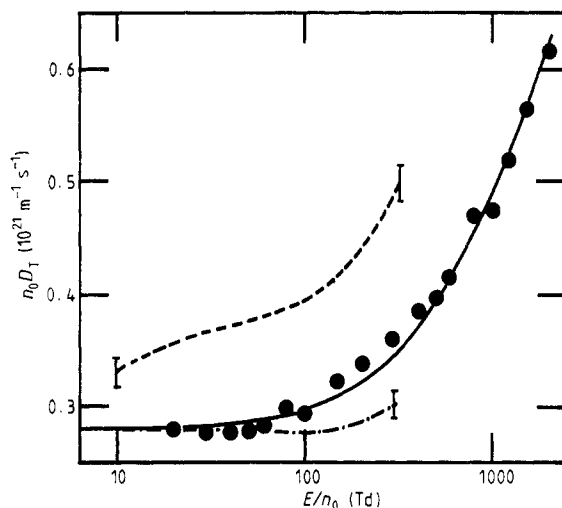
**Figure 10.** $Ne^+$–Ne reduced transverse diffusion coefficient $n_0 D_T$, at 294 K. Full curve, present values (table 4); circles, experimental values of Stefánsson (1989); broken curve, smoothed experimental values from Märk *et al* (1984) (uncorrected); chain curve, same data corrected for assumed scale error. The vertical bars indicate the experimental scatter. The experimental $D_T/\mu$ values were converted to $n_0 D_T$ values using our calculated $n_0 \mu$ values.

and by Märk *et al* (1984)†. As for the room temperature mobilities, a 2 : 1 average over the two spin states has been used for the comparison.

The transport coefficients and mean ion energies calculated from the potential A are shown in table 4.

### 4.3. Discussion

The results reported above show that it is possible to achieve agreement, within the combined uncertainties, between experimental and calculated $Ne^+$–Ne transport coefficients, using a plausible potential model with no more than three adjustable parameters.

The experimental mobilities are compatible neither with the g–u splittings reported by Cohen and Schneider (1974) nor with those of Michels *et al* (1978). In the internuclear distance region 8–10 $a_0$, the splittings for both $\Sigma$ and $\Pi$ states are well approximated by the pure asymptotic expressions, with an electron wavefunction normalisation factor $A_v = 1.90$, while the two references mentioned both seem to extrapolate to considerably lower splittings in this region.

The transport coefficients are not very sensitive to the depth $D_0$ of the potential minimum of the $Ne_2^+$ ground state molecular ion. The use of various potential models, all acceptable with regard to the values obtained for the transport coefficients, thus gave $D_0$ values varying from 0.0515 to 0.0550 au. This corresponds to dissociation energies $D_e$ from 0.050 to 0.0535 au. However, the values are in fair agreement with the experimental estimate $D_e = 0.050 \pm 0.003$ of Biondi and co-workers, and indicate that most theoretical calculations have given too shallow a minimum.

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† Märk *et al* show their $D_T/\mu$ values on a figure with a scale ranging from 0 to 100 mV. Reasonable values can only be obtained by assuming that the range should be corrected to [10,50] mV.

The relatively low sensitivity to the value of $D_0((\frac{1}{2})_u(^2P_{3/2}))$ may qualitatively be explained by the fact that the value is large compared with typical thermal energies ($kT \sim 0.001$ au at room temperature). The remaining five potential curves, however, have depths $D_0$ not far from $kT$, and the relative variations observed in these $D_0$ values with the various potential models used were typically smaller.

The potential models used here are quite crude. Thus, the mean potential $\bar{V}$ should be different for $\Sigma$ and $\Pi$ states, and the same applies to the shapes of the relative splittings $\delta V_{rel}$. However, very little information is available presently to guide in guessing what the differences might look like. The construction of more elaborate potential models should therefore be put aside until better *ab initio* calculations become available.

It is not possible to reconstruct in detail the potentials used by Cohen and Schneider (1975) in their calculation of mobilities, as they do not tell exactly how they extrapolate to large internuclear distances. This remark also applies to the transport calculations of Viehland and Hesche (1986), where the potentials of Cohen and Schneider and of Michels *et al* were tested. However, it seems clear that no reasonable extrapolation can possibly yield the mobility values found by Cohen and Schneider. The reason for their very low values may originate from their formula for the thermal energy diffusion coefficient, where the ion mass seems to have been used instead of the reduced mass. This would account for an error by a factor $\sqrt{2}$—and correcting their results with this factor yields fair agreement with the values calculated by Viehland and Hesche.

The diffusion coefficients calculated in the present work are in good agreement with the experimental values of Stefánsson (1989), and below 60 Td also with the corrected values of Märk *et al* (1984). Above 60 Td, the values of Märk *et al* are too low due to the lack of correction for end effects.

It should be remarked that all the calculations reported above were performed as if neon were a one-isotope gas, with mass number 20.183, while in fact it is a 10 : 1 mixture of the isotopes $^{20}$Ne and $^{22}$Ne. We have tried to estimate the maximum error that may arise from this approximation, and believe that the mobility values are probably not influenced by more than about 0.1%.

## 5. Conclusion

Slight adjustments of the *ab initio* He$^+$–He potentials of Maas *et al* (1976) and Metropoulos *et al* (1987), combined with a careful extrapolation to large internuclear distances, has led to calculated mobilities for He$^+$ ions in He agreeing with experimental values well inside the stated experimental accuracies. The agreement between calculated and experimental transverse diffusion coefficients is however not satisfactory at $E/n_0$ values above 500 Td, and the reasons for the disagreement are not clear.

At very large internuclear distances $R$, the gerade–ungerade potential splitting can be written as a leading asymptotic expression multiplied by a power series in $1/R$. The first term in this power series has been given by Bardsley *et al* (1975). The present study shows that for the He$^+$–He system, the power series correction is misleading if applied at $R$ values of importance for the transport properties, i.e. $R \sim 10\ a_0$ or smaller. It is then better not to apply any correction at all. This finding may possibly also apply to the heavier noble gas systems.

For the Ne$^+$–Ne system, the published theoretical potentials do not extrapolate towards the correct asymptotic forms. A simple potential model, with three adjustable parameters and acceptable asymptotic forms, was therefore used instead, and

gave agreement between calculated and experimental transport coefficients within the stated experimental uncertainties. The experimental transport coefficient included fine-structure state resolved 77–78 K mobility data, and state-averaged mobility and transverse diffusion data at 294 K and $E/n_0$ values to above 1000 Td. The transport coefficients seem to fix the values of the potential splittings at $R \sim 8$–10 $a_0$ to better than $\pm 5\%$, but are not very sensitive to the value of the potential minimum for the $Ne_2^+$ ground state ion.

For the $He^+$–He system, it was necessary to use a fully quantal scattering calculation to achieve sufficient accuracy, except at strong fields $E/n_0 > 200$ Td. For the $Ne^+$–Ne system, however, a quasiclassical approximation could be used, and we expect this to be the case also for the heavier noble gases. This greatly reduces the computation time needed, and also makes discussions of nuclear symmetry effects irrelevant.

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