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# Wannier electron capture to form doubly excited states of He and He⁻

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In this paper we present a complete account of our below-threshold semiclassical theory for the study of doubly excited states. This theory, derived by the analytic continuation of Crothers above-threshold theory, relies on a complex Bohr–Sommerfeld quantization rule in order to determine the complex eigenenergies of the high-lying doubly excited states of the negative ion He⁻ and atomic He. The 'Wannier ridge' resonant positions of He⁻ for both intrashell and intershell states are presented for $L = 0$ with an extension to include resonant states for $L = 1$ and $L = 2$, where $L$ is the total angular-momentum azimuthal quantum number of the two excited electrons. The intensities of these states have been estimated from the explicit widths given by the imaginary parts of the eigenvalue. For He**, with core charge $Z = 2$, the intrashell and intershell $S$ resonance energy positions are also presented for values of principal quantum number up to $n = 15$.

**Keywords: helium and helium-ion resonances; Wannier analytic continuation;**
**Bohr–Sommerfeld quantization rule; semiclassical JWKB analysis; complex**
**eigenenergies and relative intensities; doubly excited states**

## 1. Introduction

Electrons colliding with atoms or ions can form, at well-defined energies, compound states consisting of the target plus the incident electron. The result, in what amounts to a capture process, is the formation of non-stationary (short-lived) doubly excited states (DES) which can be viewed as resonances. In this paper the term 'resonance' is synonymous with the term 'doubly excited state' and they are used interchangeably so that a resonance is simply viewed as a temporary negative ion or temporary excited neutral atom. Common to both is the dominant role played by the electron–electron interaction most pertinent in such threshold systems. For the neutral-atom case the outer of the two excited electrons sees a positively charged core, and its motion is dominated by long-range Coulomb interactions which allow an infinite number of Rydberg series of DES to reside within the continuum between the first and second ionization thresholds. In the vicinity of the resonance, strong electron–electron interactions become increasingly important and are of great significance in the quantitative study of such DES (Oza 1986). In contrast the outermost of the two external electrons for the negative-ion case is screened from the nuclear charge by the inner electron and moves in a potential that can only support a finite number of bound states. The long series of resonances observed in negative ions (Schulz 1963; Brunt *et al.* 1977; Buckman *et al.* 1983; Buckman & Newman 1987) must therefore be formed

by a different kind of mechanism. Fano (1980) suggested a configuration in which the two electrons are on opposite sides and of comparable distance from the ion, i.e. the Wannier ridge configuration which gives rise to a long-range Coulomb field that might support a Rydberg-like series of resonances. He proposed that this configuration, considered the most important for threshold ionization (Wannier 1953), might give rise to a series of quasi-standing waves in direct analogy with the formation of Landau standing waves. Such resonances are features of localized motion along a potential ridge with reflection of the wave packets at the classical turning points of the system. A wealth of experimental and theoretical evidence exists to support this proposal (Komninos *et al.* 1987; Rau 1983; Buckman *et al.* 1983) and it is now well established that for DES of He$^-$ the highly correlated two-electron excitations manifest themselves as 'Wannier ridge resonances'. The main result of Wannier's classical threshold ionization study is the $E^{m_{12}}$ cross-section energy-dependence law where the Wannier exponent $m_{12} = 1.127, 1.056$ for core charges $Z = 1, 2$, respectively. The decreasing exponent tending towards a linear law is expected with an increasing core charge $Z$ due to the reduced effect of the electron–electron interaction. The threshold law has been confirmed semiclassically by Peterkop (1971) and quantum mechanically by Rau (1971). An absolute threshold law remained unknown until Crothers (1986) published the first absolute theoretical singlet triple-differential and integrated cross-sections for the threshold electron-impact single ionization of helium using a uniform semiclassical approximation to evaluate the final-state wave function.

In the following, we are going to consider the extension of threshold ionization theory (Crothers 1986) to below the double continuum. We will begin with a brief summary of the modified JWKB Peterkop method of Crothers (1986), to be referred to hereafter as (I), for the unstable motion of a pair of electrons along the Wannier ridge. This is extended to the near-threshold-capture excitation process

$$\text{e}^- + \text{He}(1\text{s}^{2\,1}\text{S}) \rightarrow \text{He}^-[1\text{s}\,^2\text{S}(n_1\text{s}n_2\text{s}\,^1\text{S})]^2\text{S},$$

initially for $L = 0$ and then returning to first principles and retaining angular-momentum terms we present results for $L = 1$ and $L = 2$. This below-threshold analysis is then further extended beyond the negative ion case to the following process:

$$\text{e}^- + \text{He}^+(1\text{s}\,^2\text{S}) \rightarrow \text{He}(n_1\text{s}n_2\text{s}\,^1\text{S}).$$
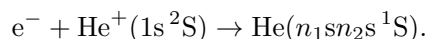
## 2. Theoretical background: the semiclassical approximation

In (I), the threshold ionization of helium by electron impact is considered by adopting the semiclassical JWKB method of Peterkop (1971) in order to produce a final-state wave function for the asymptotic escape of two electrons. This is a three-body electron–electron ion problem which is non-separable where for the case of threshold ionization the incident electron has energy just above the ionization threshold. The hyperspherical coordinates

$$\rho^2 = r_1^2 + r_2^2, \quad \alpha = \tan^{-1}(r_2/r_1), \quad \theta_{12} = \cos^{-1}(\hat{\boldsymbol{r}}_1 \cdot \hat{\boldsymbol{r}}_2), \tag{2.1}$$

are used throughout this paper and effectively describe the electron-correlated motion of the threshold processes. They define the shape of the three-body triangle converting the motion of the two electrons to that of a 'single particle' in six-dimensional

space. In this system the hyper-radius $\rho$ is the only coordinate with the dimension of length and it characterizes the RMS size of the system. The hyperspherical angle $\alpha$ is associated with the radial correlated motion of the two electrons, while the mutual polar angle $\theta_{12}$ reflects the angular correlation. In this coordinate system the two electron Schrödinger equation, in atomic units, is given as

$$\left[\frac{1}{\rho^5}\frac{\partial}{\partial\rho}\left(\rho^5\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2\sin^2\alpha\cos^2\alpha}\frac{\partial}{\partial\alpha}\left(\sin^2\alpha\cos^2\alpha\frac{\partial}{\partial\alpha}\right)\right.$$
$$\left. - \frac{L^2(\hat{\boldsymbol{r}}_1)}{\rho^2\cos^2\alpha} - \frac{L^2(\hat{\boldsymbol{r}}_2)}{\rho^2\sin^2\alpha} + X^2 + \frac{2\zeta(\alpha,\theta_{12})}{\rho}\right]\Psi = 0, \quad (2.2)$$

where $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the position vectors of the two electrons with respect to an infinitely massive proton. The total wave number $X$ is given by $X = (2E)^{1/2} = (k_1^2 + k_2^2)^{1/2}$, where $E$ is the excess of threshold energy and $\boldsymbol{k}_1, \boldsymbol{k}_2$ are the momenta of the final-state electrons 1 and 2, while, for core charge $Z = 1$, the potential is given by

$$\zeta(\alpha,\theta_{12}) = \frac{1}{\cos\alpha} + \frac{1}{\sin\alpha} - \frac{1}{(1 - \cos\theta_{12}\sin 2\alpha)^{1/2}}. \quad (2.3)$$

The incident wave vector $\boldsymbol{k}_0$ is taken as the polar axis and the collision plane as the azimuthal plane so that $\boldsymbol{r}_i$ has spherical polar angles $(\theta_i, \phi_i)$ and $\boldsymbol{k}_i$ has spherical polar angles $(\Theta_i, \Phi_i)$ with $\hat{\boldsymbol{k}}_1 \cdot \hat{\boldsymbol{k}}_2 = \cos\Theta_{12}$. The Wannier configuration, given by $\alpha = \frac{1}{4}\pi$, $\theta_{12} = \pi$, is the most important configuration for threshold escape based on the physical arguments of mutual repulsion and dynamical sharing of the residual energy. This point is a saddle point of the potential surface given in (2.3) about which the Wannier ridge expands for $\alpha = \frac{1}{4}\pi$ $\forall\theta_{12}$ and corresponds to $\boldsymbol{r}_1 = -\boldsymbol{r}_2$.

Considering the simplest case of motion when $L = 0$, equation (2.2) can be written as (Morse & Feshbach 1953)

$$\left[\frac{1}{\rho^5}\frac{\partial}{\partial\rho}\left(\rho^5\frac{\partial}{\partial\rho}\right) + \frac{1}{\rho^2\sin^2\alpha\cos^2\alpha}\frac{\partial}{\partial\alpha}\left(\sin^2\alpha\cos^2\alpha\frac{\partial}{\partial\alpha}\right)\right.$$
$$\left. + \frac{1}{\rho^2\sin^2\alpha\cos^2\alpha}\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}} + X^2 + \frac{2\zeta(\alpha,\theta_{12})}{\rho}\right]\Psi = 0. \quad (2.4)$$

Following Peterkop (1971), the JWKB semiclassical method is chosen to find approximate solutions of (2.4). The validity specifications of this approximation require that the potential is large and slowly varying, which is clearly violated as $\rho \to \infty$. A change of dependent variable is therefore adopted in (I) according to

$$\Psi = \frac{x|\sin(\alpha - \frac{1}{4}\pi)|^{1/2}}{\rho^{5/2}\sin\alpha\cos\alpha(\sin\theta_{12})^{1/2}}, \quad (2.5)$$

which introduces two 'pseudo-potentials' which are large near the significant Wannier line, increasing the propriety of the application of the JWKB ansatz

$$x = P^{1/2}\exp(-\mathrm{i}S/\hbar). \quad (2.6)$$

The phase function $S$ is the solution of the Hamilton–Jacobi equation, which is given by equation (22) of (I), and the amplitude $P$ is given by the continuity equation, given by equation (23) of (I). Realizing the physical significance of the Wannier line,

the potential $\zeta(\alpha, \theta_{12})$ is expanded, as a two-dimensional Taylor series about $\alpha = \frac{1}{4}\pi$, $\theta_{12} = \pi$, according to

$$\zeta(\alpha, \theta_{12}) = Z_0 + \tfrac{1}{2} Z_1 (\Delta\alpha)^2 + \tfrac{1}{8} Z_2 (\Delta\theta_{12})^2, \tag{2.7}$$

with

$$Z_0 = \frac{4Z - 1}{\sqrt{2}}, \quad Z_1 = \frac{12Z - 1}{\sqrt{2}}, \quad Z_2 = -\frac{1}{\sqrt{2}}, \tag{2.8}$$

where $\Delta\alpha = \alpha - \frac{1}{4}\pi$ and $\Delta\theta_{12} = \pi - \theta_{12}$. It is assumed that the deviation of the mutual polar and hyperspherical angles from their Wannier ridge values is small. Similar expansions in $S$ and $P$ are taken with the expansion of $S$ generalized to

$$S = s_0 \ln|\Delta\alpha| + s_1 \ln(\Delta\theta_{12}) + S_0(\rho) + \tfrac{1}{2} S_1(\rho)(\Delta\alpha)^2 + \tfrac{1}{8} S_2(\rho)(\Delta\theta_{12})^2. \tag{2.9}$$

The action $S$ serves to identify the direction of motion of the particles and the logarithmic terms included in (2.9) act as hallmarks of the long-range Coulomb potentials. Equations (2.7) and (2.9) are substituted into the Hamilton–Jacobi equation and the coefficients of equal powers of $\Delta\alpha$ and $\Delta\theta_{12}$ are equated. The resulting equations are solved perturbatively so that, with $s_0 = -\frac{1}{2}\mathrm{i}$ and $s_1 = \frac{1}{2}$ chosen for symmetry reasons, $S_0$ is given exactly by

$$S_0 = \int_0^\rho \mathrm{d}\tilde\rho\, \overline{w}(\tilde\rho), \tag{2.10}$$

where, with $w^2 = 2E + 2Z_0/\rho$,

$$\overline{w}^2 \simeq w^2 - w\frac{\mathrm{d}}{\mathrm{d}\rho}(\ln u_2) + \mathrm{i}w\frac{\mathrm{d}}{\mathrm{d}\rho}(\ln u_1) \tag{2.11}$$

(˜ indicates a dummy variable of integration). The remaining terms in the $S$ expansion are given by the Riccati equation

$$w\frac{\mathrm{d}S_i}{\mathrm{d}\rho} + \frac{S_i^2}{\rho^2} = \frac{Z_i}{\rho}, \quad i = 1, 2, \tag{2.12}$$

which is solved by direct analogy with the theory of Peterkop (1971) yielding

$$S_i = \rho^2 w \frac{1}{u_i}\frac{\mathrm{d}u_i}{\mathrm{d}\rho}, \quad i = 1, 2. \tag{2.13}$$

The Wannier–Peterkop functions $u_1$ and $u_2$ are given by

$$u_1 = \rho^{m_{12}}\, {}_2F_1(m_{12}, m_{12} + 1; 2m_{12} + \tfrac{3}{2}; -E\rho/Z_0), \tag{2.14}$$

$$u_2 = \rho^{m_{22}}\, {}_2F_1(m_{22}, m_{22} + 1; 2m_{22} + \tfrac{3}{2}; -E\rho/Z_0), \tag{2.15}$$

where the Wannier indices $m_{ij}$, $i, j = 1, 2$ take their usual form

$$m_{i1} = -\tfrac{1}{4} - \tfrac{1}{2}\mu_i, \quad m_{i2} = -\tfrac{1}{4} + \tfrac{1}{2}\mu_i, \tag{2.16}$$

$$\mu_i = \frac{1}{2}\left(1 + \frac{8Z_i}{Z_0}\right)^{1/2}, \tag{2.17}$$

and where the function ${}_2F_1$ is a Gauss hypergeometric function (Abramowitz & Stegun 1970). The Wannier functions, $u_1$ and $u_2$, are related to the radial and angular correlated motion of the two electrons. This can be seen by considering the set of

orbits described by $S$ which yields $u_1(\rho) = \Delta\alpha$ and $u_2(\rho) = \Delta\theta_{12}$. The final-state JWKB in-going wave function takes the form

$$\Psi_{\mathrm{f}}^{-*} = \frac{C^{1/2}\exp\{-\frac{1}{2}\mathrm{i}\ln\Delta\theta_{12} - \mathrm{i}[S_0 + \frac{1}{2}S_1(\Delta\alpha)^2 + \frac{1}{8}S_2(\Delta\theta_{12})^2]\}}{\overline{w}^{1/2}\rho^{5/2}\sin\alpha\cos\alpha}. \tag{2.18}$$

The normalization constant $C$ is found by current normalization carried out at $\rho = \infty$, which gives the asymptotic form of the normalization constant as

$$C = \frac{\pi Z_2\tanh(2\pi\operatorname{Im}m_{21})}{(2E)^{1/2}}cE^{m_{12}} \tag{2.19}$$

with

$$c = \frac{1}{2\pi}\frac{\Gamma(m_{12} + \frac{3}{2})\Gamma(m_{12} + 1)}{Z_0^{m_{12}}\Gamma(2m_{12} + \frac{3}{2})}. \tag{2.20}$$

In this threshold ionization process the two escaping electrons will have specific asymptotic directions which are represented in (I) by a factor

$$\delta(\hat{\boldsymbol{k}}_1 - \hat{\boldsymbol{r}}_1)\delta(\hat{\boldsymbol{k}}_2 - \hat{\boldsymbol{r}}_2). \tag{2.21}$$

This factor will also project out the required outgoing scattering amplitude and amounts to the inclusion of

$$Y_{l_i}^{m_i}(\hat{\boldsymbol{r}}_i)Y_{l_i}^{m_i}(\hat{\boldsymbol{k}}_i), \quad i = 1, 2 \tag{2.22}$$

for arbitrary angular-momentum states for each of the two electrons. It is argued in (I) that the inclusion of these angular-momentum terms does not affect the Hamilton–Jacobi equation for $S$ and that the change of dependent variable (2.5) will ensure a regular JWKB description of the $L = 0$ final state.

## 3. Doubly excited states of He⁻

### (*a*) *Analytic continuation to below threshold $L = 0$ states of He⁻*

We now consider the analytic continuation of the above-threshold theory to below threshold in order to calculate the complex eigenenergies $E_N$ of the high-lying doubly excited Rydberg states of He⁻ for $L = 0$ (Loughan & Crothers 1997) where the eigenvalue of the resonance takes the standard form

$$E_N = E_{\mathrm{R}}^N - \tfrac{1}{2}\mathrm{i}\Gamma_N. \tag{3.1}$$

These states are unstable and as they decay the hyperspherical angle $\alpha$ 'falls' from its Wannier ridge value $\frac{1}{4}\pi$ into the valley approaching either $0$ or $\frac{1}{2}\pi$. The real part of the eigenvalue $E_{\mathrm{R}}^N$ gives the resonance energy position while the imaginary part $\Gamma_N$ gives the lifetime of these metastable states. We view the doubly excited negative ion of helium as consisting of a positively charged core ($Z = 1$) comprising He⁺(1s) (grandparent core) with two excited electrons in a highly correlated state of energy below the single-ionization threshold of He but above the single-ionization threshold of He⁻. For the purpose of the present study, the wave function in (2.18) has been analytically continued to negative energy to represent the two excited electrons, which have positions $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, while the core electron, with position $\boldsymbol{r}_3$, is represented by the ground-state one-electron atom eigenfunction. The final-state $L = 0$

wave function, including both in-going and outgoing waves, with the Gans–Jeffreys (Gans 1915; Jeffreys 1923) connection formula applied at the classical turning point $\rho = 0$, is given by

$$
\Psi_f^{-*} = \frac{C_N^{1/2} Y_{LM}(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2) 2^{3/2} \exp(-2r_3 - \tfrac{1}{2}\mathrm{i}\ln\Delta\theta_{12})/\sqrt{\pi}}{\rho^{5/2}\sin\alpha\cos\alpha}
$$

$$
\times \frac{\sin\left[\int_0^\rho \mathrm{d}\tilde{\rho}(\omega^2 - \omega\{\ln u_2 - \mathrm{i}\ln u_1\}')^{1/2} \right.}{}
$$

$$
\frac{\left. +\tfrac{1}{2}\rho^2\omega(\ln u_1)'(\Delta\alpha)^2 + \tfrac{1}{8}\rho^2\omega\ln u_2)'(\Delta\theta_{12})^2 + \tfrac{1}{4}\pi\right]}{[\omega^2 - \omega\{\ln u_2 - \mathrm{i}\ln u_1\}']^{1/4}},
$$

$$(3.2)$$

where $'$ indicates $\mathrm{d}/\mathrm{d}\tilde{\rho}$ or $\mathrm{d}/\mathrm{d}\rho$. It is worth noting here that the exact form of $S_0$ is employed for the case of metastable bound electrons, whereas in (I) $S_0$ is approximated by equation (38) which is applicable when the ionization limit of large $\rho$ is taken. The complex eigenenergy given in (3.1) is employed so that we now have

$$
\omega^2 = 2E_N + (2Z_0)/\rho \tag{3.3}
$$

and the Wannier functions (2.14) and (2.15) take the form

$$
u_1 = \rho^{m_{12}} {}_2F_1(m_{12}, m_{12} + 1; 2m_{12} + \tfrac{3}{2}; -E_N\rho/Z_0), \tag{3.4}
$$

$$
u_2 = \rho^{m_{22}} {}_2F_1(m_{22}, m_{22} + 1; 2m_{22} + \tfrac{3}{2}; -E_N\rho/Z_0), \tag{3.5}
$$

where the indices $m_{12}$ and $m_{22}$ are given by (2.16) and (2.17). The wave function includes, for arbitrary $l_1$, $m_1$, $l_2$, $m_2$, the spherical harmonic factor $Y_{LM}(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{r}}_2)$, representing (2.22). A crucial feature of the threshold region is the $E^{1/4}$ dependence of the angular distribution; such tight angular correlation $\theta_{12} = \pi$ can be viewed, even for $L = 0$, as the ability of the individual orbital angular momenta of the two electrons to vary over a large range (Rau 1971). In this case $L = 0$ and the only restrictions on the magnitudes of the $l$ values of the individual electrons are that they should be equal and less than the individual principal quantum numbers.

Viewing the DES of He$^-$ as 'Wannier ridge resonances', where standing waves are produced as a result of wave packet reflection at the classical turning points, exponential decay of the wave function is required beyond the two transition points of this resonating system. The transition points, given by $\omega = 0$, are $\rho = 0$ and $\rho = -Z_0/E_N$. We clearly have one complex and one real transition point for this $L = 0$ problem where in the region beyond the two turning points the solution is required to be the decreasing JWKB solution, in order to satisfy the boundary conditions at 0 and $\infty$. Continuity across these points requires that on the ridge we have

$$
\int_0^{-Z_0/E_N} \mathrm{d}\rho \sqrt{\omega^2 - \omega\left(\frac{\mathrm{d}}{\mathrm{d}\rho}\ln u_2 - \mathrm{i}\frac{\mathrm{d}}{\mathrm{d}\rho}\ln u_1\right)} = N\pi + \tfrac{1}{2}\pi, \tag{3.6}
$$

which is in the form of the Bohr–Sommerfeld quantization rule. It is easily seen that $N$, a hyperspherical radial quantum number for the two excited electrons confined to the ridge, is the number of nodes of the JWKB wave function between the two turning points. In order to simplify the solution of (3.6), the dummy variable was changed according to

$$
\rho = \frac{-Z_0 x}{E_N}, \tag{3.7}
$$

Table 1. *Resonance position energies (RPEs) for $L = 0$, $n_1 = n$, $n_2 = n_1 \Rightarrow N = n_1 + n_2 - 1 = 2n-1$ and for $L = 0'$, $n_1 = n$, $n_2 = n_1 + 1 \Rightarrow N = n_1 + n_2 - 1 = 2n$ since $N = n_1 + n_2 - |l_1 - l_2| - 1$ where $L = |l_1 - l_2|$*

(The experimental values are from (a) Buckman *et al.* (1983) and (b) Buckman & Newman (1987) using their notation. The number in brackets indicates the error in the second and third decimal places.)

| | | present results RPEs (eV) | | | (a) | (b) |
|---|---|---|---|---|---|---|
| $n$ | $N$ | $L = 0$ | $N$ | $L = 0'$ | $L = 0$ | $L = 0'$ |
| 2 | 3 | 19.492 | | | 19.367 (5) | |
| 3 | 5 | 22.330 | 6 | 22.963 | 22.451 (10) | 22.881 (5) |
| 4 | 7 | 23.368 | 8 | 23.641 | 23.435 (10) | 23.667 (5) |
| 5 | 9 | 23.833 | 10 | 23.973 | 23.850 (10) | 23.983 (10) |
| 6 | 11 | 24.077 | 12 | 24.158 | 24.080 (10) | 24.176 (10) |
| 7 | 13 | 24.220 | 14 | 24.271 | 24.217 (10) | 24.288 (10) |
| 8 | 15 | 24.311 | | | 24.307 (15) | |
| 9 | 17 | 24.372 | | | 24.387 (15) | |

with the result that (3.6) becomes

$$c \int_0^1 dx \left( \frac{1}{x} - 1 \right)^{1/4} \sqrt{c^2 \left( \frac{1}{x} - 1 \right)^{1/2} - \frac{d}{dx} \ln \frac{u_2}{u_1^i}} = N\pi + \tfrac{1}{2}\pi, \qquad (3.8)$$

where

$$c = \left( \frac{-2Z_0^2}{E_N} \right)^{1/4}. \qquad (3.9)$$

Equation (3.8) has been solved numerically using the complex Newton–Raphson method. The solution involves the removal of the obvious removable singularity at the lower end-point and requires the analytic continuation of the Gauss hypergeometric function at the upper end-point. The logarithmic derivative term, in the above integrand, is divergent for $x = 1$. It was necessary to use the following analytic continuation of the Gauss hypergeometric function (Abramowitz & Stegun 1970):

$$_2F_1(a, b; d; z) = \frac{\Gamma(d)\Gamma(d - a - b)}{\Gamma(d - a)\Gamma(d - b)} {_2F_1}(a, b; a + b - d + 1; 1 - z)$$

$$+ (z - 1)^{d-a-b} \frac{\Gamma(d)\Gamma(a + b - d)}{\Gamma(a)\Gamma(b)} {_2F_1}(d - a, d - b; d - a - b + 1; 1 - z)$$

$$(|\arg(1 - z)| < \pi), \quad (3.10)$$

and to remove the removable singularity at $x = 1$ in the integral of (3.8). A similar procedure was required for the derivative of (3.8) with respect to $c$. The results obtained from this calculation are given in table 1, where they are compared with the experimental results of Buckman *et al.* (1983) and of Buckman & Newman (1987). In table 2, we compare our results (theory (a)) with those given on p. 576 of Buckman & Clark (1994).

We tentatively approach the issue of the intensity values of these states given experimentally, as the ratio of the mean peak-dip height to the mean background

Table 2. *The experimental values (the number in brackets indicates the error in the second and third decimal places) are from Buckman et al. (1983) and Buckman & Newman (1987)*

(Theory: (a) current results; (b) Rau (1983); (c) Lin & Watanabe (1987); (d) Komninos *et al.* (1987); (e) Rost & Briggs (1988); (f) Fon *et al.* (1989).)

| $n$ | $N$ | experiment | theory | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | (a) | (b) | (c) | (d) | (e) | (f) |
| 3 | 5 | 22.451 (10) | 22.330 | — | — | 22.432 | 22.774 | 22.439 |
| 4 | 7 | 23.435 (10) | 23.368 | — | — | 23.408 | 23.578 | 23.434 |
| 5 | 9 | 23.850 (10) | 23.833 | 23.857 | 23.865 | 23.843 | 23.879 | — |
| 6 | 11 | 24.080 (10) | 24.077 | 24.087 | 24.095 | 24.077 | 24.090 | — |
| 7 | 13 | 24.217 (10) | 24.220 | 24.223 | 24.230 | 24.213 | 24.219 | — |
| 8 | 15 | 24.307 (15) | 24.311 | 24.310 | 24.316 | 24.301 | 24.304 | — |
| 9 | 17 | 24.387 (15) | 24.372 | 24.369 | | 24.361 | 24.362 | — |

count of the observed resonance, by Buckman & Newman (1987). We approach the problem by considering the autoionization theory of Fano (1961), which, by detailed balance, is applicable to electron-capture DES formation. The term 'autoionization' is applied to levels produced by excitation of loosely bound electrons. Fano (1961) gives the autoionization transition-probability rate $A^a$ as being proportional to the square of the configuration-interaction matrix elements, $\langle \phi | H | \psi_\epsilon \rangle$, where for the case of autoionization the unperturbed discrete state is described by $\phi$ and the continuum wave functions are given by $\psi_\epsilon$. The familiar description of a resonance as a discrete state embedded in a continuum comes into play, so that $\phi$ corresponds to our final-state wave function $\Psi_f^{-*}$, and $\psi_\epsilon$ corresponds to the target He($1s^2\ ^1$S) wave function, $\phi_i$. We therefore seek the form of $|\langle \Psi_f^{-*} | H | \phi_i \rangle|^2$, which is found to be proportional to $|E_N|$. Therefore we take the intensity as being proportional to the product of this probability rate and the lifetime, $\frac{1}{2}\Gamma_N$, that is $|E_N|\frac{1}{2}\Gamma_N$. The results of this calculation are given in table 3.

(i) *Results and discussion*

Since the pioneering observation of the He$^-$($1s2s^2$) $^2$S resonance by Schulz (1963), resonances in the helium atom, from 19.3 eV to the ionization limit, have been studied in a variety of electron-scattering experiments. The energy dependence of reaction products, in one or more of the decay channels energetically available to the compound state, such as electrons (elastic and inelastically scattered and transmitted), decay photons, and metastable atoms, has been measured (Buckman & Clarke 1994). In the higher-energy region spanning *ca.* 22.4–24 eV many partly overlapping sharp resonance structures were observed in a number of high-resolution studies (Brunt *et al.* 1977; Keesing 1977; Buckman *et al.* 1983; Heddle *et al.* 1977; Pichou *et al.* 1976; Andrick 1979). The most extensive study of these auto-detaching states of He$^{-*}$ was made by Buckman *et al.* (1983) and later by Buckman & Newman (1987) in measurements of metastable-atom excitation. These experiments trace the occurrence of resonances for $n = 3$ to $n = 8$, where $n$ is the lower of the two principal quantum numbers $n_1$ and $n_2$. The observed resonances were classified into four prominent symmetry classes i.e $^2$S, $^2$P$^0$, $^2$D and $\bar{s}\,^2$S (Andrick 1979; Nesbet 1978; Buckman *et*

al. 1983; Brunt *et al.* 1977). The last of these classifications, proposed by Nesbet
(1978), is not considered to be associated with He$^-$ valence shells in the standard
'grandparent-type' resonance, but rather is formed by the attachment of an electron
in the polarization potential associated with the neutral excited state (parent). The
lowest three (in energy) of these four symmetry classes were further classified (Brunt
*et al.* 1977; Nesbet 1978; Andrick 1979) as intrashell resonances, with $n_1 = n_2$ while
the final resonance was of the intershell type, with $n_1 \neq n_2$. Buckman & Newman
(1987) traced all four of these features to $n = 6$ and the $^2$S, $^2$P and $\bar{s}\,^2$S features to
$n = 8$ with an additional tentative observation of the lowest $^2$S feature at $n = 9$. In
this section we are concerned with the $L = 0$ $^2$S and $\bar{s}\,^2$S states which we describe,
in the interest of brevity, in terms of the more conventional, though admittedly less
accurate, notation used by Buckman *et al.* (1983). The most widely accepted termi-
nology used for such high-lying highly correlated DES are the $K$, $T$ and $A$ quantum
numbers proposed by Lin (1986). In this scheme the states currently being considered
are represented by

$$\alpha(K,T)_\beta^{A\ 2S+1}L^\pi = {}_{n_2}(n_1 - 1, 0)_{n_1}^0\,{}^1\mathrm{S}^\mathrm{e}, \tag{3.11}$$

where $\alpha$, denoted by $n$ in Lin's (1986) notation, is the principal quantum number
of the outer electron and $\beta$, denoted by $N$ in Lin's (1986) notation, is the principal
quantum number of the inner electron. In table 1 we present our resonance energy
positions for both intrashell and intershell $^2$S states and compare them with exper-
iments. Our calculated eigenvalues are found to correspond to those of Buckman *et
al.* (1983) and Buckman & Newman (1987) for

$$N = n_1 + n_2 - L - 1, \tag{3.12}$$

with the lower of the $^2$S features given by $N$ values where $n_1 = n_2 = n$, while those
of the higher $^2$S features correspond to values of $N$ for $n_1 = n$, $n_2 = n_1 + 1$. Thus
our classification is consistent with Nesbet (1978) and an equal sharing of energy,
$n_1 = n_2$, or almost equal sharing, $n_2 = n_1 + 1$, is obtained. This reflects the energy
repartitioning to increase stability expected in Wannier ridge features. Essentially
any partitioning of $E$, into $(E_1, E_2)$ where $E = E_1 + E_2$, is possible; equally well,
any partitioning of $N + L + 1$, into $(n_1, n_2)$ couples where $N + L + 1 = n_1 + n_2$, is
possible. As $n$ increases, motion becomes increasingly localized near $\theta_{12} = \pi$ as the
electrons move to minimize their mutual repulsive energy, and strong mixing of higher
$l$ values is expected. However, we are concerned with the partitioning relevant to the
central resonance peak while recognizing that other $(n_1, n_2)$ couples are involved in
the broadening of the resonance. In table 2, we compare our results (theory (a))
with those of Rau (1983) (b) and Lin & Watanabe (1987) (c), both of which are
semiempirical, being based on generalized Rydberg-quantum-defect formulae; with
Komninos *et al.* (1987) (d), which is also a multiconfiguration Hartree–Fock theory;
with Rost & Briggs (1988) (e), which is a diabatic molecular treatment; and finally
with Fon *et al.* (1989) (f), who conducted an R-matrix calculation. For $n \in [6, 9]$, our
results lie within experimental error. For $n \in [3, 5]$, our results are a little on the low
side by 0.111, 0.057 and 0.007, respectively. For $n \in [3, 4]$ the R-matrix theory (e)
(Fon *et al.* 1989) gives the best agreement. By the very semiclassical nature of our
near-threshold analysis, the accuracy of our results at the higher $n$ values would be
expected to exceed that for the lower $n$ values.

In table 3 we compare our relative intensities, given by $|E_N|\frac{1}{2}\Gamma_N$, with those of
Buckman & Newman (1987). For $N = 13, 15, 17$, that is for the highest Rydberg

Table 3. *Relative intensity values for $L = 0$ resonances*

(The experimental values (the number in brackets indicates the error in the last and second last decimal places) are from Buckman & Newman (1987).)

| | relative intensity | | |
|---|---|---|---|
| $N$ | experiment | $\frac{1}{2}\Gamma_N * |E_R^N - \frac{1}{2}\mathrm{i}\Gamma_N|$ | ratio |
| 5 | 0.53(1) | 0.0050 | 0.0094 |
| 7 | 0.048 (1) | 0.00099 | 0.021 |
| 9 | 0.010 5(2) | 0.00029 | 0.028 |
| 11 | 0.002 1(3) | 0.00011 | 0.052 |
| 13 | 0.001 1(1) | 0.000049 | 0.045 |
| 15 | 0.000 54(12) | 0.000024 | 0.044 |
| 17 | 0.000 30(12) | 0.000013 | 0.043 |

Table 4. *Variation in intensity as a function of $N$*

| author | prediction |
|---|---|
| Feagin & Macek (1984) | $I_N \sim N^{-5.254} = N^{-3-2m_{12}}$ |
| Rau (1984) | $I_N \sim N^{-6.254}$ |
| Heim & Rau (1995) | $I_N \sim N^{-6.5}$ |
| Buckman & Newman (1987) | $I_N \sim N^{-5.2 \pm 0.7}$ |
| present | $I_N \sim N^{-5.0}$ |

states, and for $n = 7, 8, 9$, we see that the ratio of the our Wannier results and the experimental results has reached a stable converged value, namely $4.4(\pm 0.1) \times 10^{-2}$ for $N \in [13,17]$, which embraces an error tolerance of less than 3%. We have also investigated the variation in the intensities of these resonances as a function of $N$. We determined that for $N \to \infty$, $E_R^N \sim N^{-2}$ and $\Gamma_N \sim N^{-3}$, with the net effect that $I_N \sim N^{-5}$. This $N^{-2}$ and $N^{-3}$ behaviour is to be expected, for instance by taking the small $x$ behaviour of $u_1$ and $u_2$ in (3.8), evaluating as a sum of two $_3F_2$ hypergeometric functions and analytically continuing via Barnes complex contour integrals. This and other theoretical and experimental results are given in table 4. These are the results for higher $N$ values, with our result varying within the error bars of Buckman & Newman (1987) for lower $N$ values, namely $N^{-4.89}$ for $N \in [21,29]$ and $N^{-4.88 \pm 0.01}$ for $N \in [13,17]$.

### (b) Analytic continuation to below threshold $L = 1$ and $L = 2$ states of He$^-$

We now consider the analytic continuation of (I) to below threshold for $L = 1$ and $L = 2$ states of He$^-$ (Loughan & Crothers 1998). Our perception of (He$^-$)$^{**}$ is, as for the $L = 0$ case, in terms of the grandparent model of Schulz (1973). We return to the Schrödinger equation (2.2) where (Morse & Feshbach 1953)

$$L^2(\hat{\boldsymbol{r}}_i) = -\left[\frac{1}{\sin\theta_i}\frac{\partial}{\partial\theta_i}\left(\sin\theta_i\frac{\partial}{\partial\theta_i}\right) + \frac{1}{\sin^2\theta_i}\frac{\partial^2}{\partial\phi_i^2}\right] \quad i = 1, 2, \qquad (3.13)$$

and retain these angular-momentum terms. For states with $L \neq 0$, the shape of the three-body triangle is, as usual, defined by the hyperspherical coordinates $\rho, \alpha, \theta_{12}$

and the orientation in space of this triangle is described by three Euler angles. Following Selles *et al.* (1987) we employ the Euler angles of Breit (1930) $(\phi_i, \theta_i, \psi_B)$; $i = 1, 2$ and for $M = 0$ we proceed with the ansatz

$$\Psi = f(\rho, \alpha, \theta_{12}) P_L(\cos\theta_1), \qquad (3.14)$$

where $P_L$ is the Legendre polynomial. On symmetrizing this becomes

$$\Psi = f(\rho, \alpha, \theta_{12}) P_L(\cos\theta_1) \pm \tilde{f}(\rho, \alpha, \theta_{12}) P_L(\cos\theta_2), \qquad (3.15)$$

where the upper (lower) sign is for the singlet-symmetric (triplet-antisymmetric) case. The ˜ marks the interchanged function $\tilde{f}(\boldsymbol{r}_1, \boldsymbol{r}_2) = f(\boldsymbol{r}_2, \boldsymbol{r}_1)$ and particle exchange results in $\Delta\theta_{12} \to \Delta\theta_{12}$ and $\Delta\alpha \to -\Delta\alpha$. We therefore obtain the following equation for the hyperspherical part of the wave function $f$:

$$\left[\frac{1}{\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} + \frac{1}{\rho^2\sin^2 2\alpha}\frac{\partial}{\partial\alpha}\sin^2 2\alpha\frac{\partial}{\partial\alpha} + \frac{4}{\rho^2\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}\right.$$
$$\left. + 2E + \frac{2\zeta(\alpha,\theta_{12})}{\rho} - \frac{2L(L+1)}{\rho^2}\right]f = 0, \quad (3.16)$$

where the factor of 2 in the last term comes from $\sec^2\alpha$ evaluated at $\alpha = \frac{1}{4}\pi$. The substitution of (3.13) and (3.14) into (2.2) also results in the cross term

$$\frac{4\sin\theta_1(-\sin\theta_1\cos\theta_2 + \cos\theta_1\sin\theta_2\cos(\phi_1-\phi_2))}{\rho^2\sin\theta_{12}}\frac{P'_L(\cos\theta_1)}{P_L(\cos\theta_1)}\frac{\partial f}{\partial\theta_{12}}, \qquad (3.17)$$

where $'$ indicates $\mathrm{d}/\mathrm{d}(\cos\theta_1)$. This term can be shown, in common with the equivalent term in equation (3) of Roth (1972), to vanish on the Wannier line ($\alpha = \frac{1}{4}\pi, \theta_{12} = \pi$) where the singularity due to $\sin\theta_{12}$ in the denominator requires the use of L'Hospital's rule with the numerator expressed in terms of the following identity:

$$\cos\theta_{12} = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\phi_1-\phi_2). \qquad (3.18)$$

This term, which notably contains Euler angles, is therefore neglected and it follows that on the Wannier ridge $f = \tilde{f}$. Equation (3.16) is equivalent to equation (8) of (I) if we take the $w$ term to be $L$-dependent according to

$$w^2 = 2E_N + \frac{2Z_0}{\rho} - \frac{2L(L+1)}{\rho^2}. \qquad (3.19)$$

Thus the Riccati equation given in (2.12), which is reduced to a linear second-order equation by removing the nonlinear $S_i^2$ term with the substitution given by equation (2.13), becomes

$$\rho^2 w^2 \frac{\mathrm{d}^2 u_i}{\mathrm{d}\rho^2} + \left(2\rho w^2 - Z_0 + \frac{2L(L+1)}{\rho}\right)\frac{\mathrm{d}u_i}{\mathrm{d}\rho} = \frac{Z_i u_i}{\rho} \quad i = 1, 2. \qquad (3.20)$$

Following (I), we set

$$u_i = \rho^{m_i} F_i(\rho) \quad i = 1, 2, \qquad (3.21)$$

so that the equation for the $\rho$-dependent function $F$ becomes

$$[2E_N\rho^2 + 2Z_0\rho - 2L(L+1)]F_i''$$
$$+ \left[4(m_i+1)E_N\rho + (4m_i+3)Z_0 - \frac{2(2m_i+1)L(L+1)}{\rho}\right]F_i'$$
$$+ \left[2m_i(m_i+1)E_N - \frac{2m_i^2 L(L+1)}{\rho^2}\right]F_i = 0, \qquad (3.22)$$

where $m_i$ is given as both roots in (2.16). This is a linear differential equation of the Heun type (Ronveaux 1997), which has four regular singular points at $\rho = 0, \infty$ and $\rho_{\pm}$ that are the solutions of $w^2 = 0$ where

$$\rho_{\pm} = \frac{-Z_0 \pm \sqrt{Z_0^2 + 4E_N L(L+1)}}{2E_N}. \tag{3.23}$$

Detailed knowledge of the Heun equations is limited so an approximate solution to (3.22) is required. We simplify matters by assuming that $\rho$ is of the order of $1/|E_N|$, which is certainly reasonable, so that all the non-azimuthal terms in the coefficients of (3.22) are of the order of $1/|E_N|$. The result is that, for the threshold limit of $E_N \to 0$, we may neglect the $L$-dependent terms. Therefore we can approximate the solutions of (3.22) with those obtained for the $L = 0$ case. For $L = 0$ with $F = F(-E\rho/Z_0)$, a differential equation with three regular singular points obtains and takes the form of the Gauss-hypergeometric differential equation resulting in the Wannier–Peterkop functions given in equations (2.14) and (2.15). The asymptotic form of the final-state wave function for He$^-$ with $L \neq 0$ is given by (3.2) with two significant changes. The first being the obvious change in the integration limits from $0 \to \rho$ to $\rho_+ \to \rho$, since the classical turning point moves away from the origin for $L$-dependent states. The second is the change in the form of $\omega$ which according to (3.19) is now $L$-dependent. The Langer modification term (Langer 1937), $-1/4\rho^2$, has also been considered where it has been found to be cancelled by two terms, namely $-15/4\rho^2$ and $4/\rho^2$, resulting from the substitution of equation (2.5) into equation (2.4). The $L$-dependent form of $\omega$ further complicates the solution of the Bohr–Sommerfeld quantization expression

$$\int_{\rho+}^{\rho-} d\rho \sqrt{w^2 - w\left(\frac{d}{d\rho} \ln u_2 - i\frac{d}{d\rho} \ln u_1\right)} = N\pi + \tfrac{1}{2}\pi, \tag{3.24}$$

which is completely analogous to (3.6) with two complex transition points. Following the method for the $L = 0$ case, we simplify (3.24) with a change of dummy variable according to

$$\rho = \frac{-(Z_0 + Zx)}{2E_N}, \tag{3.25}$$

where

$$Z = \sqrt{Z_0^2 - 2c^2 L(L+1)} \tag{3.26}$$

and

$$c = \sqrt{-2E_N}. \tag{3.27}$$

Equation (3.24) then becomes

$$Z \int_{-1}^{1} dx \sqrt{\varpi^2 - \frac{c}{Z}\varpi\left(\frac{d}{dx} \ln \frac{u_2}{u_1^i}\right)} = c(N + \tfrac{1}{2})\pi, \tag{3.28}$$

where

$$\varpi^2 = -1 + \frac{2Z_0}{Z_0 + Zx} - \frac{2c^2 L(L+1)}{(Z_0 + Zx)^2}, \tag{3.29}$$

which has been solved numerically for $c$ by the complex Newton–Raphson method.

Table 5. *Resonance position energies (RPEs) for* $(1s\,^2S(n_1sn_2p\,^3P^0))\,^2P$, $L = 1$, $M = 0$,
$n_1 = n$, $n_2 = n_1 \Rightarrow N = 2n - \frac{1}{2}(17^{1/2} - 1) - 1$

(The experimental values are from Buckman *et al.* (1983). The number in brackets indicates the
error in the second and third decimal places.)

| | RPEs (eV) | |
|---|---|---|
| $n$ | present results | experiment |
| 3 | 22.639 | 22.600 (10) |
| 4 | 23.518 | 23.518 (10) |
| 5 | 23.915 | 23.907 (10) |

Table 6. *Resonance position energies (RPEs) for* $(1s\,^2S(n_1sn_2d\,^1D^e))\,^2D$, $L = 2$, $M = 0$,
$n_1 = n$, $n_2 = n_1 \Rightarrow N = 2n - 4$

(The experimental values are from Buckman *et al.* (1983). The number in brackets indicates the
error in the second and third decimal places.)

| | RPEs (eV) | |
|---|---|---|
| $n$ | present results | experiment |
| 3 | 22.715 | 22.660 (10) |
| 4 | 23.544 | 23.579 (10) |
| 5 | 23.927 | 23.952 (10) |
| 6 | 24.133 | 24.144 (15) |
| 7 | 24.256 | 24.261 (15) |

### (i) *Results and discussion*

The results obtained from this calculation for the $L = 1$ and $L = 2$ resonant energy
positions are given in tables 5 and 6, respectively. They have been compared with the
experimental results of Buckman *et al.* (1983) using their notation where, in the now
standard notation (Lin 1986), these states are represented by $_{n_2}(n_1 - 1, 0)^0_{n_1}\,^3P^0$,
$^1D^e$. It has been found that the calculated eigenvalues for both $L = 1$ and $L = 2$
resonant states correspond to those of experiment for

$$N = 2n - \mathcal{L} - 1, \tag{3.30}$$

where for $L = 1$, $\mathcal{L} = \frac{1}{2}(-1 + \sqrt{17})$ and for $L = 2$, $\mathcal{L} = 3$ and where $2n = n_1 + n_2$ in
line with the intrashell classification as discussed in § 3 a. Thus for $L = 0$ and $L = 2$
we have an integer hyperspherical azimuthal quantum number but for $L = 1$ the
mapping of $2L(L + 1)$ to $\mathcal{L}(\mathcal{L} + 1)$ in the Bohr–Sommerfeld quantization rule results
in an irrational hyperspherical azimuthal quantum number.

The agreement with experiment is good and improves for higher values of $N$. In
particular, for $L = 1$ and $n = 4$ or 5 and for $L = 2$ and $n = 6$ or 7, experiment and
theory agree within experimental error. This is to be expected due to the semiclas-
sical nature of the calculation and our perturbative solution of the Heun differential
equation.

These closely spaced P and D resonances are close together and overlap so that
the width for a given $E_R^N$ is smeared by the neighbouring resonances (Andrick 1979).
As such, in our search for the resonance energy position we took the narrowest
(central and highest) peak, corresponding to the complex eigenenergy $E_N$ closest

Table 7. *Average widths and associated energy positions for* $(1s^2\,S(n_1sn_2d\,^1D^e))\,^2D$, $L = 2$,
$M = 0$, $n_1 = n$, $n_2 = n_1 \Rightarrow N = 2n - 4$ *(units are eV)*

| $n$ | $\Gamma^a$ | $E_{\Gamma^a}$ | experiment |
|---|---|---|---|
| 4 | 0.3401 | 23.578 | 23.579 |
| 5 | 0.2313 | 23.952 | 23.952 |
| 6 | 0.1252 | 24.144 | 24.144 |
| 7 | 0.0680 | 24.261 | 24.261 |

to the real axis. On allowing $\Gamma_N$ to tend to zero a convergence limit was reached yielding the energy positions tabulated in tables 5 and 6. In order to determine $\Gamma_N$ for these 'smeared' overlapping states a sum over the unobserved final states (Feagin & Macek 1984) was taken in order to obtain an average width $\Gamma^a$. Since our intensity is taken as being proportional to $\frac{1}{2}\Gamma_N|E_N|$, this sum takes the form

$$\Gamma^a = \frac{1}{n}\sum_{i=1}^{n}\Gamma_N^i|E_N^i| \bigg/ \frac{1}{n}\sum_{i=1}^{n}|E_N^i|. \tag{3.31}$$

In table 7 we present the $\Gamma^a$ values for the $^2D$ case. The lower limit of the sum is determined by the convergence limit for a given $n$, while the upper limit is determined by the position of the neighbouring observed resonance. Admittedly the choice of the upper limit is somewhat arbitrary in that the extent of the overlapping is not definite. Nevertheless, with an appropriate choice of upper limit the energy positions $E_{\Gamma^a}$ corresponding to width $\Gamma^a$ show excellent agreement with experiment. Convergence difficulties have restricted the application of (3.31) to higher $n$ values of the $^2D$ case only.

## 4. Doubly excited states of He

In this section we apply the below-threshold theory for $L = 0$ developed in § 3 *a* to the DES of atomic helium. In direct analogy with the He$^-$ case we consider the electron capture by the 'parent' He$^+$(1s) to form the DES of atomic He with the grandparent core He$^{++}$. The energy of the incident electron lies below the first ionization potential of He but above the first ionization potential of He$^+$. For He$^{**}$ the Coulomb potential experienced by the excited electrons is such that it can support an infinite Rydberg series with electron correlations dominating the motion close to the resonance region. We consider the two excited electrons in terms of our semiclassical Wannier wave function. The continuum between the first and second ionization thresholds of the helium atom has been investigated theoretically in a number of diverse studies (Fukuda *et al.* 1987; Grujić & Simonović 1995; Ho 1986; Ho & Calloway 1986; Muller *et al.* 1994; Oza 1986; Rost & Briggs 1988). This work was initiated by Madden & Codling (1963), who, in a photoabsorption experiment, were the first to observe doubly excited autoionizing states of atomic helium. Subsequent photoabsorption experiments (Domke *et al.* 1996; Zubek *et al.* 1989) have yielded further information about states of $^1P$ symmetry, with electron-impact experiments (Brotton *et al.* 1997; Hicks & Cromer 1975) revealing the full spectrum of the S, P, D, F, G states. An infinite number of Rydberg series of autoionizing states exist within the continuum. However, these studies have predominantly concentrated on

the lower Rydberg series which converge to the $He^+$ $n = 2$–$6$ thresholds with the more recent diabatic molecular approach of Rost & Briggs (1989) producing intrashell S resonance positions for $n \leqslant 15$. Here we present intrashell and intershell S resonance energy positions for the higher quantum numbers $5 \leqslant n \leqslant 15$, with the semiclassical limitations of our theory producing poor results for lower $n$ values. Clearly, the core charge in this case is $Z = 2$, which reflects the increasing Coulomb attraction of the $He^{++}$ core over the $Z = 1$ $He^+$ core. This gives the three-body potential (2.3) as

$$\zeta(\alpha, \theta_{12}) = \frac{2}{\cos \alpha} + \frac{2}{\sin \alpha} - \frac{1}{(1 - \cos \theta_{12} \sin 2\alpha)^{1/2}}, \tag{4.1}$$

which is expanded according to (2.7), where, from (2.8),

$$Z_0 = 7/\sqrt{2}, \quad Z_1 = 23/\sqrt{2}, \quad Z_2 = -1/\sqrt{2}. \tag{4.2}$$

Retaining $Z$ in the semiclassical analysis gives the Wannier indices (2.16) and (2.17):

$$m_{i1} = -\tfrac{1}{4} - \tfrac{1}{2}\mu_i, \quad m_{i2} = -\tfrac{1}{4} + \tfrac{1}{2}\mu_i, \tag{4.3}$$

where

$$\mu_1 = \frac{1}{2}\sqrt{\frac{100Z - 9}{4Z - 1}}, \quad \mu_2 = \frac{1}{2}\sqrt{\frac{4Z - 9}{4Z - 1}}. \tag{4.4}$$

The method used to determine the complex eigenenergies $E_N$ (3.1) is completely analogous to the procedure followed in § 3 a with the Wannier indices and charges calculated for $Z = 2$. To avoid repetition the reader is referred to equations (3.6)–(3.10).

The results from the present calculation, given in tables 8 and 9, show poor agreement with the available experimental and theoretical results for values of $n$ up to $n = 7$, for both the intrashell ($n_1 = n_2$) and intershell ($n_1 \neq n_2$) states. Other theories such as the complex-coordinate rotation theory (Ho 1986; Ho & Calloway 1986), close-coupling method (Oza 1986) and hyperspherical approach (Fukuda *et al.* 1987) have produced accurate energy positions for lower $n$ but require greater numerical effort for higher values of principal quantum number. Rost & Briggs (1988) have produced intrashell energy positions for $n \leqslant 15$ using an adiabatic molecular potential. For $n \leqslant 7$ these results are in excellent agreement with Ho's highly accurate results (Ho 1986; Ho & Calloway 1986). We have compared our resonance energy positions for $He^{**}$ $^1S^e$ intrashell states for $7 \leqslant n \leqslant 15$ with those of Rost & Briggs (1988). We find the results for $7 \leqslant n \leqslant 10$ to be in agreement to within 10% and for $n \geqslant 11$ to within 4%. Thus agreement with other theory is seen to improve for increasing $n$. Rost & Briggs (1988) have employed a simple hydrogenic wave function, of the form $e^{-\alpha(r_1 + r_2)}$, which is clearly symmetric in $r_1$ and $r_2$. Thus this approach does not allow for the determination of resonance positions where the energy of the two electrons is not evenly distributed, i.e. only energy positions for intrashell states can be calculated.

## 5. Conclusion

In summary, we have analytically continued the above-threshold Wannier quantal ionization theory of (I) to below threshold for Wannier quantal DES. We have presented results for $^2S$ and $\bar{s}\,^2S$ DES of $He^-$, where for the principal series, $n_1 = n_2 = n$

Table 8. *Resonance position energies (RPEs) for He: $L = 0$, $n_1 = n$, $n_2 = n_1 \Rightarrow N = 2n - 1$; other theory (a) Rost & Briggs (1988, 1989)*

| | | | RPEs (au) | |
|---|---|---|---|---|
| $ns^2$ | $(K,T)^A$ | $N$ | present results | (a) |
| $7s^2$ | $(6,0)^+$ | 13 | 0.073 667 | 0.066 716 |
| $8s^2$ | $(7,0)^+$ | 15 | 0.055 528 | 0.051 207 |
| $9s^2$ | $(8,0)^+$ | 17 | 0.043 310 | 0.040 538 |
| $10s^2$ | $(9,0)^+$ | 19 | 0.034 702 | 0.032 887 |
| $11s^2$ | $(10,0)^+$ | 21 | 0.028 415 | 0.027 365 |
| $12s^2$ | $(11,0)^+$ | 23 | 0.023 688 | 0.023 205 |
| $13s^2$ | $(12,0)^+$ | 25 | 0.020 044 | 0.019 64 |
| $14s^2$ | $(13,0)^+$ | 27 | 0.017 179 | 0.016 95 |
| $15s^2$ | $(14,0)^+$ | 29 | 0.014 885 | 0.014 78 |

Table 9. *Resonance position energies (RPEs) for He: $L = 0$, $n_1 = n$, $n_2 = n_1 + 1 \Rightarrow N = 2n$*

| | | | RPEs (au) | |
|---|---|---|---|---|
| $n_1 s n_2 s$ | $(K,T)^A$ | $N$ | present results | other theories |
| 5s6s | $(4,0)^+$ | 10 | 0.122 978 | 0.109 64[b] |
| 6s7s | $(5,0)^+$ | 12 | 0.086 212 | 0.078 65[a] |
| 7s8s | $(6,0)^+$ | 14 | 0.063 650 | 0.059 9[a] |
| 8s9s | $(7,0)^+$ | 16 | 0.048 856 | |
| 9s10s | $(8,0)^+$ | 18 | 0.038 652 | |
| 10s11s | $(9,0)^+$ | 20 | 0.031 325 | |
| 11s12s | $(10,0)^+$ | 22 | 0.025 891 | |
| 12s13s | $(11,0)^+$ | 24 | 0.021 753 | |
| 13s14s | $(12,0)^+$ | 26 | 0.018 529 | |
| 14s15s | $(13,0)^+$ | 28 | 0.015 970 | |
| 15s16s | $(14,0)^+$ | 30 | 0.013 906 | |

[a]Fukuda *et al.* (1987).
[b]Ho (1986).

and $N = 2n - 1$, $L = 0$, while for the subsidiary series, $n_2 = n_1 + 1 = n + 1$ and $N = 2n$, $L = 0'$, in the notation of Buckman *et al.* (1983). We have extended this theory to $L = 1$ and $L = 2$ $^2P^0$ and $^2D$ states where, with the inclusion of angular-momentum terms evaluated on the Wannier ridge, an irrational principal quantum number was obtained for $L = 1$, namely $N = 2n - \frac{1}{2}(17^{1/2} - 1) - 1$, while for $L = 2$, $N = 2n - 4$. The calculated resonance positions were found to be in good agreement with experiment, the agreement increasing for higher $n$. This is to be expected due to the semiclassical nature of the calculation and certainly much can be done to improve our description of the initial state. The width and intensity of these states were also considered using the imaginary parts of the calculated complex eigenenergies that give directly the lifetime of these Wannier doubly excited Rydberg states. This is unique in that other theories address the problem of resonance position only. We also applied the below-threshold analysis for $L = 0$ to the DES of He, where a simple change in the magnitude of the core charge produced reasonable results for high values of $n$. As far as we know the intershell energies are the first to be presented

for these higher quantum numbers; other theories are restricted by computational demands at the higher end of the spectrum.

There is no doubt that this below-threshold theory is an exciting development in the Wannier description of DES and reinforces the above-threshold theory as a fully fledged quantal treatment of ionization. Most significant for future work are the advances made for $L \neq 0$ states. Throughout the years the difficulties encountered manifested themselves as triplet triple-differential cross-sections for threshold ionization that were much too large, but recent progress has produced improved results (Crothers 1986; Carruthers & Crothers 1992). We are now confident that the additional angular-momentum term in $\omega$, namely $2L(L + 1)/\rho^2$, is the required amendment to our above-threshold theory, where preliminary investigations are more than promising (Loughan 1998). It is worth noting that the cross term given in (3.17) should not be completely dismissed due to its disappearance on the Wannier ridge. Closer inspection, with symmetrization for P and D states, shows that it vanishes specifically for ${}^3$P and ${}^1$D states. There is, of course, room for many further improvements, such as the inclusion of exchange to improve results for the lower quantum numbers.

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