Theoret. Chim. Acta (Berl.) 51, 311—322 (1979)

THEORETICA CHIMICA ACTA


# Uniform Approximate Franck–Condon Matrix Elements for Bound-Continuum Vibrational Transitions*

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Franck–Condon matrix elements are calculated approximately for vibrational transitions of a diatomic molecule from a bound electronic potential curve to a purely repulsive curve. The bound states are approached by exactly normalized Miller–Good wavefunctions uniform in both turning points. For the continuum wavefunction a single turning point uniform Airy approximation is taken. The resulting Franck–Condon matrix element is approximately done in closed form with the help of a new canonical integral for a product of harmonic oscillator wavefunctions and Airy functions. The degree of agreement with a closed form exact result is qualitatively discussed for transitions from the ground state of a Morse curve to the continuum of a particular repulse exponential curve.

**Key words:** Franck–Condon factors – Bound-continuum emission – Semiclassical matrix elements – Excimer lasers

## 1. Introduction

Prominent examples for the importance of bound-to-continuum Franck–Condon factors are given by the vacuum ultraviolet emission spectra of excited state rare gas dimers (excimers). Here, the "second continuum" is usually attributed to bound–continuum transitions from low vibrational states of either or both of the lowest two bound potential curves to the repulsive ground state curve of the dimer [1]. The inverse process, the continuum-to-bound transition falls into the domain of radiative recombination.

Many useful approximate expressions for Franck–Condon (FC) matrix elements [2–7] have been developed by adopting semiclassical or uniform semiclassical

* Dedicated to Professor Hermann Hartmann on the occasion of his 65th birthday.

0040-5744/79/0051/0311/$02.40

techniques. By construction, most of these expressions are the better valid the larger is the number of nodes involved on the bound state wavefunction.

The aim of this paper is to derive approximate FC matrix elements just for transitions from the lowest, or the first few excited vibrational states to the continuum of a repulsive potential curve, a situation typically met in excimer systems (see also Fig. 1). The detailed plan of this paper is as follows: In Sect. 2 we derive an accurate closed-form expression for the normalization constant of two-turning point uniform Miller–Good bound state wavefunctions in an arbitrary potential well [8]. This expression seems to have not appeared in the literature before. For the ground state in a Morse well this normalization constant is used to demonstrate the excellent accuracy of Miller–Good functions at the two turning points of the well.

In Sect. 3, the FC integral is formed of Miller–Good bound state- and single-turning point uniform continuum wavefunctions. Assuming that the Miller–Good function is slowly varying with the internuclear separation compared to the continuum function, this FC integral can be done in closed form.

Finally, in Sect. 4 the accuracy of the resulting FC matrix element is qualitatively checked with the help of an exact expression derived for the FC matrix element of a Morse ground state and the continuum state of a repulsive exponential curve with the same exponential parameter.

## 2. Normalization of Miller–Good Bound State Functions

Following the work of S. C. Miller and R. H. Good, Jr. [8], the wavefunction of the $n$th bound state of two particles with reduced mass $m$ and interacting via an arbitrary anharmonic potential well $V_1(x)$ which gives rise to the two turning points $x_1, x_2, x_1 < x_2$ can be mapped on harmonic oscillator functions according to

$$\varphi_n(x) = N_n[z_1'(x)]^{-1/2}\, e^{-(1/2)z_1^2(x)} H_n(z_1(x)), \qquad z_1'(x) = \frac{dz_1(x)}{dx}, \tag{1}$$

where the mapping function $z_1(x)$ is determined by solving

$$[z_1'(x)]^2[2n + 1 - z_1^2(x)] = \frac{2m}{\hbar^2}[E_1(n) - V_1(x)] \tag{2}$$

with the boundary conditions

$$z_1(x_{1_{(2)}}) = \mp\sqrt{2n+1}, \qquad V_1(x_{1_{(2)}}) = E_1(n). \tag{3}$$

The binding energies $E_1(n)$ are fixed by the implicit equation (WKB-condition)

$$\int_{x_1}^{x_2} dx \sqrt{\frac{2m}{\hbar^2}[E_1(n) - V_1(x)]} = \pi(n + \tfrac{1}{2}), \quad n = 0, 1, 2, \ldots. \tag{4}$$

In order to satisfy the normalization condition

$$\int_{-\infty}^{+\infty} dx \varphi_n^2(x) = 1, \tag{5}$$

Miller and Good propose a numerical procedure to do the integral (5). That this is in fact not necessary is stated by the following formula, which seems not to have been given previously in the literature,

$$N_n = \left\{\frac{[m/\hbar^2][dE_1(n)/dn]}{2^n n!\,\sqrt{\pi}}\right\}^{1/2}. \tag{6}$$

In (6), $dE_1(n)/dn$ has to be calculated from (4) after continuation to real values of $n$.

To prove (6), we note that the $\varphi_n(x)$ in (1) for arbitrary real values of $n$ are given by the parabolic cylinder functions $D_n(z)$ [8, 9],

$$\varphi_n(x) = N_n[z_1'(x)]^{-1/2}2^{n/2}D_n(z_1(x)\sqrt{2}) = N_n 2^{n/2}[z_1'(x)]^{-1/2}\psi_n(z_1), \tag{7}$$

which in the variable $x$ solve the Schrödinger Equation

$$\left\{\frac{d^2}{dx^2} + \frac{2m}{\hbar^2}[E_1(n) - V_1(x) - \tilde{V}_1(x)]\right\}\varphi_n(x) = 0 \tag{8}$$

with the potential correction

$$\tilde{V}_1(x) = \frac{\hbar^2}{2m}[z_1'(x)]^{1/2}\frac{d^2}{dx^2}\{[z_1'(x)]^{-1/2}\}. \tag{9}$$

The essence of the Miller–Good approach is the neglect of the Schwarzian derivative contribution (9) in Eq. (8). For proving (6) one certainly needs not to do better, and hence, after omitting $\tilde{V}_1$, one finds from (8) and the equation obtained from (8) by taking a partial derivative with respect to $n$, the approximate Wronski relation [10–11]

$$\frac{2m}{\hbar^2}\frac{dE_1(n)}{dn}\int_{-\infty}^{+\infty} dx\varphi_n^2(x) \simeq \left[\frac{\partial\varphi_n(x)}{\partial n}\frac{\partial\varphi_n(x)}{\partial x} - \varphi_n(x)\frac{\partial^2\varphi_n(x)}{\partial x\,\partial n}\right]_{x=-\infty}^{x=+\infty}. \tag{10}$$

Changing in the Wronskian from the variable $x$ to $z_1 = z_1(x)$ and omitting contributions from the boundaries at $x = \pm\infty$, which vanish exactly if $n$ tends to a positive integer or zero, one finally obtains from (10)

$$\frac{2m}{\hbar^2}\frac{dE_1(n)}{dn}\int_{-\infty}^{+\infty} dx\varphi_n^2(x) \simeq 2^n N_n^2\left[\frac{\partial\psi_n(z)}{\partial n}\frac{\partial\psi_n(z)}{\partial z} - \psi_n(z)\frac{\partial^2\psi_n(z)}{\partial z\,\partial n}\right]_{z=-\infty}^{z=+\infty} \tag{11a}$$

$$= N_n^2 2^{n+1}\int_{-\infty}^{+\infty} dz\psi_n^2(z), \tag{11b}$$

because the $\psi_n(z)$ in (7) solve the differential equation

$$\left\{\frac{d^2}{dz^2} + 2n + 1 - z^2\right\}\psi_n(z) = 0 \tag{12}$$

and this leads to the Wronski relation between (11a) and (11b). Thus, in the limit of positive integer values of $n$, Eqs. (11b), (7), (1) and

$$\int_{-\infty}^{+\infty} dx\, e^{-x^2}H_n^2(x) = 2^n n!\,\sqrt{\pi}$$

precisely yield Eq. (6).

Inspection of Eqs. (2), (3) and (6) shows that the values of the bound state functions (1) at the two turning points $x_1$, $x_2$ can easily be calculated if $x_1$, $x_2$ and $E_1(n)$ in (4) can be found in closed form. Assuming $x_1$, $x_2$ and $dE_1(n)/dn$ to be known, Taylor expansion of (2) at $x_{1_{(2)}}$ gives

$$z_1'(x_{1_{(2)}}) = \left\{\frac{\mp mV_1'(x_{1_{(2)}})}{\hbar^2\sqrt{2n+1}}\right\}^{1/3}. \tag{13}$$

For the Morse potential with the minimum separation $x_m$ and $\alpha > 0$,

$$V_1(x) = D[e^{-2\alpha(y-1)} - 2\,e^{\alpha(y-1)}], \quad y = \frac{x}{x_m}, \tag{14}$$

one finds from (4) the exact term formula

$$E_1(n) = -D\left[1 - \frac{n+\frac{1}{2}}{d}\right]^2, \quad 0 \leqslant n \leqslant n_{\max} \leqslant d - \tfrac{1}{2}, \tag{15}$$

$$d = \frac{x_m}{\hbar\alpha}\sqrt{2mD}, \tag{16}$$

and from (6)

$$N_n = \frac{\alpha}{x_m}\left(\frac{d-n-\frac{1}{2}}{2^n n!\sqrt{\pi}}\right)^{1/2}, \tag{17}$$

so that (13) yields

$$z_1'(x_{1_{(2)}}) = \frac{\alpha}{x_m}\left[\frac{d^2(\eta \pm \eta^2)}{\sqrt{2n+1}}\right]^{1/3}, \tag{18}$$

where

$$\eta = \left[1 - \left(1 - \frac{n+\frac{1}{2}}{d}\right)^2\right]^{1/2}. \tag{19}$$

It is instructive to compare the values of the Miller–Good function (1) for the ground state $n = 0$ at the two turning points $x_1$, $x_2$

$$x_m^{1/2}\alpha^{-1/2}\varphi_0(x_{1_{(2)}}) = \left(\frac{d-\frac{1}{2}}{e\pi^{1/2}}\right)^{1/2} d^{-1/3}\eta^{-1/6}(1 \pm \eta)^{-1/6} = f_{1_{(2)}}(d) \tag{20}$$

with the corresponding values

$$g_{1_{(2)}}(d) = \frac{e^{-d(1\pm\eta)}[2d(1 \pm \eta)]^{d-1/2}}{[\Gamma(2d-1)]^{1/2}} \tag{21}$$

of the exact Morse ground state function

$$x_m^{1/2}\alpha^{-1/2}\varphi_{0\,\mathrm{exact}}(x) = \frac{e^{-dt}(2\,dt)^{\,d-1/2}}{[\Gamma(2d-1)]^{1/2}}, \quad t = e^{-\alpha(y-1)}, \quad y = \frac{x}{x_m} \tag{22}$$

at $x = x_1, x_2$. The excellent agreement of $f_{1_{(2)}}(d)$ with $g_{1_{(2)}}(d)$ is shown in Table 1 for various values of $d$. Note also the asymmetry between $f_1$ and $f_2$, which reflects the anharmonicity of the Morse well (14) especially at low values of $d$.

**Table 1.** Values of the exact Morse ground state function $g_{1(2)}(d)$, Eq. (21) and the corresponding values of the Miller–Good function $f_{1(2)}(d)$, Eq. (20), for various values of the Morse parameter $d$, Eq. (16)

| $d$ | $g_1$ | $f_1$ | $g_1$ | $f_2$ |
|---|---|---|---|---|
| 1 | 0.2989 | 0.2974 | 0.4527 | 0.4613 |
| 2 | 0.4367 | 0.4360 | 0.5662 | 0.5683 |
| 3 | 0.5128 | 0.5123 | 0.6294 | 0.6304 |
| 4 | 0.5677 | 0.5673 | 0.6759 | 0.6766 |
| 5 | 0.6113 | 0.6111 | 0.7136 | 0.7140 |
| 6 | 0.6480 | 0.6478 | 0.7455 | 0.7459 |
| 8 | 0.7079 | 0.7077 | 0.7985 | 0.7988 |
| 10 | 0.7564 | 0.7563 | 0.8421 | 0.8422 |
| 15 | 0.8499 | 0.8498 | 0.9272 | 0.9273 |
| 20 | 0.9210 | 0.9210 | 0.9930 | 0.9930 |
| 25 | 0.9792 | 0.9792 | 1.0473 | 1.0473 |
| 30 | 1.0290 | 1.0290 | 1.0940 | 1.0940 |
| 35 | 1.0727 | 1.0727 | 1.1352 | 1.1352 |

It should be stressed however, that in order to calculate the mapping $z_1(x)$ and its derivative $z_1'(x)$ for values of $x$ away from the turning points $x_1$, $x_2$ one is in general forced to set up numerical routines for solving the implicit mapping equations given in [8]. That this can be done quite efficiently is obvious and will be shown by examples in a subsequent publication.

## 3. Approximate Calculation of the FC Matrix Element

In this section FC matrix elements are to be evaluated approximately for transitions from one of the lower vibrational states in an excimer curve to the continuum of a purely repulsive ground state curve $V(x)$, a situation typically as shown in Fig. 1. The lower repulsive potential curve $V(x)$ has only a single turning point and hence the continuum wave function $\psi_E(x)$ at energy $E$ above $V = 0$[1] may very well be approximated by the uniformly valid Airy-function expression [12–13]

$$\psi_E(x) = \sqrt{\frac{2m}{\hbar^2}}\left[\frac{dz(x)}{dx}\right]^{-1/2}\mathscr{A}i(-z(x)), \tag{23}$$

where the mapping function $z(x)$ satisfies

$$\left[\frac{dz(x)}{dx}\right]^2 z(x) = \frac{2m}{\hbar^2}[E - V(x)], \tag{24}$$

and

$$z(x_0) = 0 \tag{25}$$

[1] The continuum energy $E$ is normalized such that $E = 0$ coincides with $V(x) = 0$ at $x = +\infty$.

at the turning point $x_0$ defined by

$$E = V(x_0). \tag{26}$$

In contrast to Eq. (2), (24) can easily be solved for $z$, *viz.*

$$z(x) = \begin{cases} \left[\frac{3}{2}\int_{x_0}^{x} dt\sqrt{\frac{2m}{\hbar^2}[E - V(t)]}\right]^{2/3}, & \text{for } x_0 \leqslant x \leqslant +\infty \\ -\left[\frac{3}{2}\int_{x}^{x_0} dt\sqrt{\frac{2m}{\hbar^2}[V(t) - E]}\right]^{2/3}, & \text{for } -\infty \leqslant x \leqslant x_0. \end{cases} \tag{27}$$

The continuum function $\psi_E(x)$ in (23) is energy normalized according to

$$\int_{-\infty}^{+\infty} dx \psi_{E'}^*(x)\psi_E(x) = \delta(E' - E) \tag{28}$$

which can be seen from the behaviour at large values of $x$, [14],

$$\psi_E(x) \xrightarrow[x\to\infty]{} \sqrt{\frac{2m}{\pi\hbar^2 k}} \sin(kx + \delta), \quad k = \frac{1}{\hbar}\sqrt{2mE}, \tag{29}$$

$$\delta = \frac{\pi}{4} - \frac{k}{2}\int_0^{\infty} dt t \frac{d}{dt}\left\{\ln\left(1 - \frac{V(x(t))}{E}\right)\right\}, \quad t^2 = x^2\left[1 - \frac{V(x)}{E}\right]. \tag{30}$$

From Eqs. (1) and (23) one obtains the FC matrix element

$$M_n(E) = \int_{-\infty}^{+\infty} dx \varphi_n^*(x)\psi_E(x) = \sqrt{\frac{2m}{\hbar^2}} N_n \int_{-\infty}^{+\infty} dx \left(\frac{dz_1}{dx}\right)^{-1/2}\left(\frac{dz}{dx}\right)^{-1/2} \times e^{-z_1^2/2} H_n(z_1) \mathscr{A}i(-z), \tag{31}$$

which would yield very accurate results if the integration would be carried out numerically. Examples of this kind as well as for bound–bound and continuum–continuum transitions will be presented in forthcoming publications.

The aim now is to show that if the bound state part $\varphi_n(x)$ in (31) is sufficiently slowly varying in $x$ compared with the continuum part $\psi_E(x)$, the integral (31) can be done in a simple approximation. A typical situation of this kind is depicted in Fig. 1. The ground state function in the upper Morse well varies in $x$ so slowly that the continuum function of the lower repulsive curve averages out essentially all contributions to the integral (31) away from the turning point of the lower curve. Adopting this random phase argument, one may thus change in (31) from the variable $x$ to $z(x)$ (cf. (27)), expand the integrand around $z = 0$, i.e. $x = x_0$, and obtain the approximate form

$$\bar{M}_n(E) = \sqrt{\frac{2m}{\hbar^2}} N_n \frac{[z_1'(x_0)]^{-1/2}}{[z'(x_0)]^{3/2}} \int_{-\infty}^{+\infty} dz\, e^{-1/2(\rho + \sigma z)^2} H_n(\rho + \sigma z)\mathscr{A}i(-z) \tag{32}$$

with

$$\rho = z_1(x_0), \qquad \sigma = \left.\frac{dz_1}{dz}\right|_{z=0} = \frac{z_1'(x_0)}{z'(x_0)}. \tag{33}$$

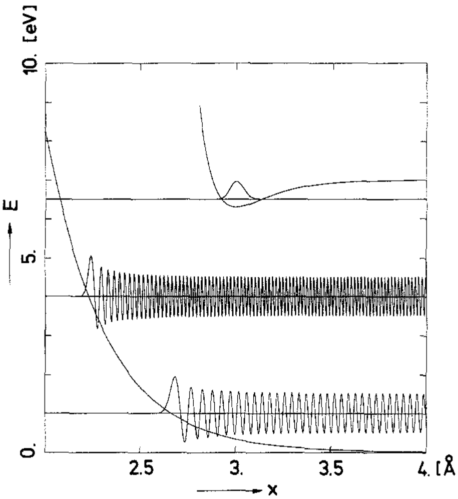


**Fig. 1.** Potential curves and wavefunctions for bound-to-continuum transitions in an excimer system (Xe–Xe). The upper curve is a Morse potential and the lower curve is an exponential potential

The "canonical" integral in (32) can be done in closed form as is shown in Appendix 1. For brevity, the result is given for $n = 0$ only, *viz.*

$$\bar{M}_0(E) = \frac{2}{\hbar}\sqrt{m\pi}N_0\frac{[z_1'(x_0)]^{-1/2}}{[z'(x_0)]^{3/2}\sigma}\exp\left(\frac{\rho}{2\sigma^3}+\frac{\sigma^{-6}}{12}\right)\mathscr{A}i\left(\frac{\rho}{\sigma}+\frac{\sigma^{-4}}{4}\right). \tag{34}$$

## 4. Comparison with an Exact FC Matrix Element

If the repulsive, lower curve in Fig. 1 is the exponential function

$$V(x) = V_0\, e^{-\beta(x/x_m)}, \quad \beta > 0, \tag{35}$$

the exact solution $\psi_E(x)$ of the Schrödinger equation is well known [15]. Energy normalized according to (28), (29), $\psi_E(x)$ becomes

$$\psi_E(x) = \frac{2}{\pi}\left\{\frac{mx_m}{\hbar^2\beta}\sinh\left(\frac{2\pi a}{\beta}\right)\right\}^{1/2}K_{2ia/\beta}\left(\frac{2b}{\beta}\exp\left(-\frac{\beta x}{2x_m}\right)\right), \tag{36}$$

where $K_\nu(z)$ is a modified Bessel function [9] and

$$a = \frac{x_m}{\hbar}\sqrt{2mE}, \qquad b = \frac{x_m}{\hbar}\sqrt{2mV_0}. \tag{37}$$

With the exact ground state function (22) of the Morse well (14) one thus obtains, after introducing $z = 2d\exp[-\alpha(x/x_m - 1)]$ as integration variable, the FC matrix element

$$M_0(E) = \frac{2x_m}{\pi\hbar}\left\{\frac{m\sinh(2\pi a/\beta)}{\alpha\beta\Gamma(2d-1)}\right\}^{1/2}\int_0^\infty dz z^{d-3/2}\,e^{-z/2}K_{2ia/\beta}(\zeta z^\mu), \tag{38}$$

where

$$\zeta = \frac{2b}{\beta} e^{-\beta/2}(2d)^{-\beta/2\alpha} \tag{39}$$

and

$$\mu = \frac{\beta}{2\alpha}. \tag{40}$$

There are two special values of $\mu$ for which the integral in (38) can be expressed in closed form in terms of higher transcendental functions, namely $\mu = \frac{1}{2}$ and $\mu = 1$. The case $\mu = 1$ can be done by use of the Laplace transform given on page 315 of [9]. The value $\mu = 1$ or $\beta = 2\alpha$ however would correspond to a quite steep lower curve, which is unrealistic in excimer systems and hence is not considered here. For $\mu = \frac{1}{2}$ or $\beta = \alpha$ one finds from [9] p. 313 the exact formula

$$M_0(E) = \frac{2x_m}{\pi\alpha\hbar\zeta}\left\{\frac{m \sinh(2\pi a/\beta)}{\Gamma(2d-1)}\right\}^{1/2} 2^{d-1} e^{\zeta^2/4}\left|\Gamma\left(d - \frac{1}{2} + i\frac{a}{\alpha}\right)\right|^2 W_{1-d,i(a/\alpha)}\left(\frac{\zeta^2}{2}\right). \tag{41}$$

Such a nice-looking closed form result is however of little value if a *stable* numerical algorithm to tabulate Whittaker's function in (41) is not available. We had precisely this experience, when we first tried to calculate $W_{-\delta,i\rho}(r)$ for realistic parameter values like $\delta = 25$, $\rho = 20$ and $r = 128$ by application of a numerical routine published by Luke [16], pp. 252. I regret that we therefore have to fall back on a stopgap, the uniform approximation to $W_{-\delta,i\rho}(r)$ presented in Appendix 2, which will be used for a qualitative test of expression (34).

In detail, we have applied two simple approximations for the mapping function $z_1(x)$ and its derivative $z_1'(x)$ instead of solving (2) and (3) for the ground state of the Morse well (14) accurately, i.e.

$$\begin{aligned} \bar{z}_1(x) &= \frac{-1}{\eta}\left[\exp\left[-\alpha\left(\frac{x}{x_m} - 1\right)\right] - 1\right], \\ z_1'(x) &= \frac{\alpha}{x_m} d^{2/3}\eta^{1/3} \exp\left[-\frac{\alpha}{3}\left(\frac{x}{x_m} - 1\right)\right], \end{aligned} \tag{42}$$

$$\tilde{z}_1(x) = \frac{\alpha}{\eta}\left(\frac{x}{x_m} - 1\right), \qquad \tilde{z}_1'(x) = \frac{\alpha}{\eta x_m}, \tag{43}$$

where $\eta$ is defined by (19).

Approximation (42) is correct at the two turning points

$$x_{2(1)} = x_m - \frac{x_m}{\alpha}\ln(1 \mp \eta), \tag{44}$$

and (43) arises on replacing the Morse well (14) by the harmonic potential

$$V(x) = \frac{m\omega^2}{2}(x - x_m)^2 - D, \quad \omega^2 = \frac{2\alpha D}{m x_m^2}. \tag{45}$$

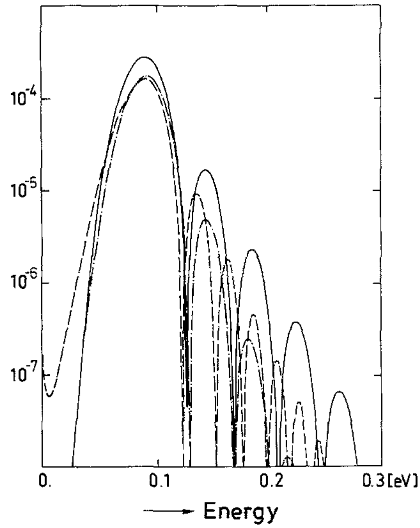


**Fig. 2.** The squared expressions (41) and (34) calculated from (42) or (43) are plotted versus $E$ in eV as the full, the dashed and the dot-dashed line respectively. All squared matrix elements are multiplied by the factor $\hbar^2/mx_m^2$

The turning point of the lower curve (35) is according to (26) at

$$x_0 = \frac{x_m}{\beta} \ln \left(\frac{V_0}{E}\right). \tag{46}$$

With (42), (43), (46) and (33), $\overline{M}_0(E)$ in (34) can be evaluated. One should recall that (42) and (43) are only approximate solutions of (2) and hence a comparison with the exact expression (41) for $\beta = \alpha$ can be only qualitative. In Fig. 2 the quantity $(\hbar^2/mx_m^2)[M_0(E)]^2$ obtained from (41) and evaluated as described in Appendix 2 is plotted as the full line versus the energy $E$ in eV. The corresponding expressions found from (34) by using either (42) or (43) are shown as the dashed resp. the dot-dashed line. The parameters $\alpha$, $d$, $V_0$ and $x_m$ in (14), (16) and (35) have been chosen according to $\alpha = 14$, $d = 26$, $V_0 = 10^5$ eV and $x_m = 3$ Å. One notes that the different approximations to $z_1(x)$ and $z_1'(x)$, (42) and (43) tend to the exact expression (41) at different energies. This indicates that if a numerically exact solution of (2) is used instead of (42) or (43), the approach (34) should be accurate over a large range of energies [17]. That this conjecture is in fact correct, will be shown in a subsequent publication.

*Acknowledgement.* The author is grateful to R. Wanik for his continuous help during the numerical calculations.

## Appendix 1

To calculate the "canonical" integral (32) it is worth while to consider the case $n = 0$ first

$$\mathscr{K}_0(x, y) = \int_{-\infty}^{+\infty} dz\, e^{-1/2(x+yz)^2} \mathscr{A}i(-z). \tag{47}$$

With

$$\mathscr{A}i(-z) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt \exp\left[i\left(\frac{t^3}{3} - zt\right)\right] \tag{48}$$

in (47) the $z$-integration can be done

$$\mathscr{K}_0(x, y) = \frac{1}{y\sqrt{2\pi}}\int_{-\infty}^{+\infty} dt \exp\left(i\frac{t^3}{3} + ixyt - \tfrac{1}{2}y^2t^2\right)$$

and this integral can be transformed into the representation (48) by the substitution $t = u - (i/2y^2)$

$$\mathscr{K}_0(x, y) = \frac{1}{y\sqrt{2\pi}}\int_{-\infty}^{+\infty} du \exp\left[\frac{iu^3}{3} + iu\left(\frac{x}{y} + \frac{1}{4y^4}\right)\right],$$

which yields the result

$$\mathscr{K}_0(x, y) = \frac{\sqrt{2\pi}}{y}\exp\left(\frac{x}{2y^3} + \frac{1}{12y^6}\right)\mathscr{A}i\left(\frac{x}{y} + \frac{1}{4y^4}\right). \tag{49}$$

For $n = 0, 1, 2, 3, \ldots$ the integral (32)

$$\mathscr{K}_n(x, y) = \int_{-\infty}^{+\infty} dz\, e^{-1/2(x+yz)^2} H_n(x + yz)\mathscr{A}i(-z) \tag{50}$$

can be obtained from

$$F(t) = \sum_{n=0}^{\infty} \mathscr{K}_n(x, y)\frac{t^n}{n!} = \int_{-\infty}^{+\infty} dz\, e^{2(x+yz)t - t^2}\, e^{-1/2(x+yz)^2}\mathscr{A}i(-z) \tag{51}$$

because of

$$e^{2wt - t^2} = \sum_{n=0}^{\infty} H_n(w)\frac{t^n}{n!}. \tag{52}$$

The integral (51) is easily done by use of (49) and one finds after Taylor expansion of the resulting $F(t)$ with the help of (52) and some straightforward algebra

$$\mathscr{K}_n(x, y) = \frac{\sqrt{2\pi}}{y}\exp\left(\frac{x}{2y^3} + \frac{1}{12y^6}\right)\sum_{k=0}^{n}\binom{n}{k} i^k H_k\left(\frac{i}{2y^3}\right)\left(\frac{-2}{y}\right)^{n-k}$$
$$\times\, \mathscr{A}i^{(n-k)}\left(\frac{x}{y} + \frac{1}{4y^4}\right) \tag{53}$$

where

$$\mathscr{A}i^{(m)}(z) = \frac{d}{dz}\mathscr{A}i^{(m-1)}(z), \qquad \mathscr{A}i^{(0)}(z) = \mathscr{A}i(z). \tag{54}$$

## Appendix 2

The Whittaker function $W_{-\delta,i\rho}(r)$, $\delta > 0$, $\rho > 0$, $r \geqslant 0$, solves the differential equation [9]

$$\left(\frac{d^2}{dr^2} - \frac{1}{4} - \frac{\delta}{r} + \frac{\frac{1}{4} + \rho^2}{r^2}\right)W_{-\delta,i\rho}(r) = 0 \tag{55}$$

and has the asymptotic behaviour

$$W_{-\delta,i\rho}(r) \xrightarrow[r\to\infty]{} e^{-r/2}r^{-\delta}\left[1 + O\left(\frac{1}{r}\right)\right]. \tag{56}$$

To get rid of the singularity of (55) at $r = 0$, one may transform according to [19]

$$r = e^x, \qquad W_{-\delta,i\rho}(r) = e^{x/2}\mathscr{W}(x), \tag{57}$$

and apply a uniform Airy approximation [18] to the differential equation resulting from (55). This approach is thus uniformly valid for $-\infty \leqslant x \leqslant +\infty$, or $0 \leqslant r \leqslant +\infty$. After some calculation, finally transforming back to the variable $r$ and matching with (56) one finds

$$W_{-\delta,i\rho}(r) = \sqrt{2\pi}\, e^c\left[\frac{r^2 t(r)}{r^2/4 + \delta r - \rho^2}\right]^{1/4}\mathscr{A}i(t(r)) \tag{58}$$

$$c = \delta - \frac{\delta}{2}\ln(\delta^2 + \rho^2) - \rho\left[\frac{\pi}{2} + \arcsin\left(\frac{\delta}{\sqrt{\rho^2 + \delta^2}}\right)\right] \tag{59}$$

$$t(r) = \begin{cases} [\frac{3}{2}f(r)]^{2/3} & \text{for } r_1 \leqslant r \leqslant +\infty \\ -[\frac{3}{2}g(r)]^{2/3} & \text{for } 0 \leqslant r \leqslant r_1 \end{cases} \tag{60}$$

$$r_1 = 2(\sqrt{\delta^2 + \rho^2} - \delta) \tag{61}$$

$$f(r) = \sqrt{\frac{r^2}{4} + \delta r - \rho^2} + \delta\,\mathrm{arccosh}\left(\frac{\delta + r/2}{\sqrt{\delta^2 + \rho^2}}\right) + \rho\left\{\arcsin\left(\frac{2\rho^2 - \delta r}{r\sqrt{\delta^2 + \rho^2}}\right) - \frac{\pi}{2}\right\} \tag{62}$$

$$g(r) = -\sqrt{\rho^2 - \frac{r^2}{4} - \delta r} + \delta\left\{\arcsin\left(\frac{\delta + r/2}{\sqrt{\delta^2 + \rho^2}}\right) - \frac{\pi}{2}\right\} + \rho\left\{\ln\left(\frac{2\rho^2}{r} - \delta + \frac{2\rho}{r}\sqrt{\rho^2 - \delta r + \frac{r^2}{4}}\right) - \frac{1}{2}\ln(\delta^2 + \rho^2)\right\} \tag{63}$$

This approximation differs from [18] because more attention is paid to the behaviour of $W_{-\delta,i\rho}(r)$ at $r = 0$.

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*Received December 23, 1978*