

ELECTRONIC INTERACTION IN THE FREE ELECTRON MODEL
INCORPORATING A FINITE NUMBER OF POTENTIAL
DISCONTINUITIES. PART I THEORY

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Two methods for approximating free electron wave functions in cases involving potential wells or barriers are discussed. These are further employed to generate expressions for evaluating the Coulomb exchange and repulsion integrals between free-electron molecular orbitals. The method is tested by application to the calculation of the electronic states of divinylborane.

Introduction

The free electron model of conjugated molecules has been independently incorporated by Ham and Rudenberg [1] and by Olszewski [2] into an antisymmetrised molecular orbital scheme capable of yielding results which correlate well with experimental electronic spectra. However one objection to the method is that the potential is assumed to be uniform throughout the molecule and the core eigen-energies and electronic interaction integrals are calculated on this basis. This assumption may be reasonably appropriate for a hydrocarbon, but it is clearly not true for a heteroatomic system. In the calculation of the core Hamiltonian matrix elements it is possible to make some allowance for the presence of heteroatoms by the inclusion of subsidiary potential wells [3] or barriers [4] which are step functions and the retaining walls may also be considered finite so as to allow for ionisation of the molecules [5]. However the electronic interaction integrals may only be calculated easily from the wave functions of the simple linear well. This approximation may not be too serious when there are few barriers and they are low or narrow because a limited number of energy levels will be affected but when these conditions do not hold the energies of the symmetric wave functions may be considerably modified [4]. It is the problem of allowing for a non-uniform potential which we wish to consider in this paper.

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The simple one dimensional infinite well gives rise to a set of wave functions which satisfy the Schrödinger equation, *i.e.*,

$$\psi_n = \frac{1}{\sqrt{L}} \cos \frac{n\pi z}{2L} \quad n = 1, 3, 5 \dots$$

and

$$\psi_n = \frac{1}{\sqrt{L}} \sin \frac{n\pi z}{2L} \quad n = 2, 4, 6 \dots$$

$$E_n = n^2 h^2 / 32mL^2. \quad (1)$$

These functions alone are not suitable for calculation of the energy levels of a well containing barriers (as in Figure 1(a)).

In order to satisfy the wave equation in each region different analytic forms of the wave functions are required, hence

$$\psi_{1,5} = Ae^{\pm\gamma z} \quad z < -L, \quad z > L$$

$$\gamma = \sqrt{H(V-E)} \quad H = 8\pi^2 m/h^2 = 2a.u.$$

$$\psi_{2,4} = Be^{iaz} + Ce^{-iaz} \quad -L < z < -a,$$

$$\alpha = \sqrt{HE} \quad a < z < L.$$

and finally,

$$\psi_3 = De^{+\beta z} \quad -a < z < +a$$

$$\beta = \sqrt{H(V_0-E)}. \quad (2)$$

This regional dependence of the eigenfunctions means that no single one will describe the electronic motion overall. The energies lying below the barrier may be readily obtained because the following quantum conditions must be satisfied, *i.e.* for the symmetric levels

$$\begin{aligned} & \alpha/\gamma \cos \alpha (L-a) + \sin \alpha (L-a) \\ & = K \left\{ \left[\frac{e^{\beta(L+a)} - e^{\beta(L-a)}}{e^{-\beta(L-a)} - e^{-\beta(L+a)}} \right] e^{-\beta(L-a)} + e^{\beta(L-a)} \right\} \end{aligned}$$

where

$$K = \frac{\cos \alpha (L-a) \left(\alpha + \frac{\beta \alpha}{\gamma} \right) + \sin \alpha (L-a) (\beta - \alpha^2/\gamma)}{2 \beta e^{\beta(L-a)}}$$

whilst for the antisymmetric levels

$$\alpha/\gamma \cos \alpha(L-a) + \sin \alpha(L-a) = -2Ke^{\beta L/2} \sinh \beta a. \quad (3)$$

These levels constitute the core eigenenergies in the A.S.F.E.M.O. theory [4]. Because of the form of the potential in Fig. 1(a) the symmetry properties of the functions remain unchanged from those of the simple case *i.e.* they are alternately symmetric and anti-symmetric to the inversion operation.

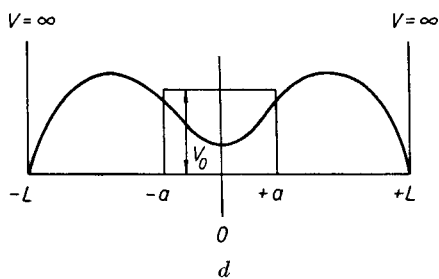
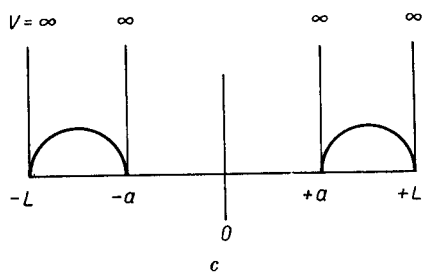
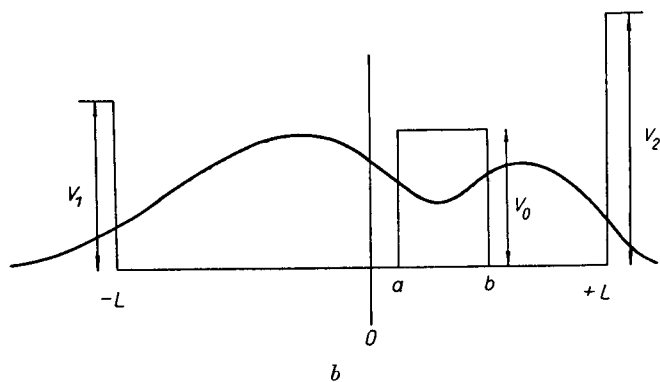
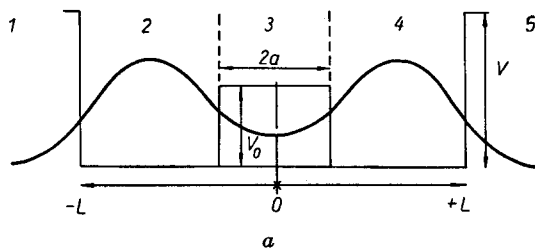


Fig. 1. Potential forms for Free-electron systems

If the molecule is considered as a long, thin cylinder then in three dimensions the total π -electron wave function is the product of three separate functions, thus [2]

$$\psi_q^\pi(r, \varphi, z) = A(1/L)^{1/2} \cos q\pi z/2L J_1(kr) \cos \varphi$$

or

$$\psi_p^\pi(r, \varphi, z) = A(1/L)^{1/2} \sin p\pi z/2L J_1(kr) \cos \varphi$$

(or in "reduced" form (*i.e.* $r \rightarrow 0$))

$$\psi_{p,q}^\pi(\varphi, z) = \sqrt{2/R(\pi L)^{1/2}} \sin \text{ or } \cos(p, q\pi z/2L) \times \cos \varphi.$$

The unit order Bessel function $J_1(kr)$, is antisymmetric to inversion through the origin, φ is the azimuthal rotation angle. Since each variable, φ, r, z , is independent, that part of the total eigenfunction may be re-expressed as a different function of that variable. The particular one which is of concern here is that which governs wave propagation along the molecular chain. A single set of eigenvalues determines the form of the z -wave function in each potential region and satisfies the continuity conditions at the boundaries.

It would be convenient to represent the eigenfunctions in the variable z by a single functional form which held for all regions of the well and we now discuss two ways in which this may be achieved.

Methods and results

Method 1. Expression as a Fourier series

Now the z -functions are piecewise continuous with no ordinary discontinuities within the well and furthermore possess right and left hand derivatives at every interior point. It follows that we may express any such eigenfunction as a separate, convergent, Fourier series in each section and according to Fourier's theorem the component series must converge to the same values as the common boundaries of the regions. However a difficulty arises because a Fourier series may only be defined for a function which is sectionally continuous on a finite interval; a wave function such as in Figure 1(a) is clearly asymptotic to the z -axis outside the well. Two ways of circumventing this problem are, *a*) an increasing exponential included in the "exterior" function so that it vanishes at some point outside the molecule. This introduces a further quantum condition *b*) the wave function may be curtailed at some finite point outside the region. The latter is simpler and, in practice, should be equally precise. The Fourier series of period $2L$ which expresses $f(z)$ in each region is

$$f(z) \approx \frac{1}{2} A_0 + \sum_{n=1}^{\infty} A_n \cos n\pi z/L + B_n \sin n\pi z/L \quad (5)$$

and the "overall" series for the well with k regions is thus,

$$f(z) \approx \frac{1}{2} \sum_{r=1}^k A_{0r} + \sum_{r=1}^k \sum_{n=1}^{\infty} A_{nr} \cos n\pi z/L + B_{nr} \sin n\pi z/L. \quad (6)$$

Because this is of the same form as (5) it means that only one Fourier series is required for the whole problem whatever the size of the system.

Simplifications arise when the function to be expanded is either symmetric or anti-symmetric to inversion of the variable z for then only the cosine series or the sine series respectively is needed. Moreover in these cases we need only expand $f(z)$ over half the well and generation of the total series simply requires this to be doubled. However, for an unsymmetrical potential as in Figure 1(b) the complete series is required for each region.

Fouriers theorem asserts that the function converges on $\frac{1}{2} [f(L-0)+f(-L+0)]$ at the extremes of the interval. This will not affect the case where the potential is symmetric but otherwise (Fig. 1b) the rate of exponential decay of the wave function at each side of the well will differ. Hence in order to ensure minimum error the cut-off point should be selected as that which makes the value of wave function with the smallest exponent negligible.

Convergence of the series.

The series converges in the ordinary sense and the Fourier coefficients are final at every stage. It is, of course, desirable to avoid an excessive number of terms in the series and it will generally be possible to do this because of the sinusoidal behaviours of the wave function in some parts of the well. A number of advantages accrue from expressing the wave function in this way,

a) the component functions are the basic sine and cosine functions of the simple linear well with period $2L$.

b) discontinuities in the wave function produce no difficulties as the components of the series are always continuous and have continuous gradients. Hence, providing the function is piecewise continuous, the series converges from the right and left-hand on any discontinuity in $f(z)$ or $f'(z)$ and, in this way, we may approach as closely as we please to the point of discontinuity, *e.g.* the wave function in figure 1(c) which is sinusoidal in the potential troughs and vanishes on the infinite walls may be expressed as one function over the whole $(L, -L)$ region.

c) Perhaps most important of all, the method is almost independent of the initial size of the problem because there is only one "overall" Fourier series for a system with any number of potential discontinuities. The electronic interaction problem thus reduces to that for the simple potential box.

A Fourier representation is useful further where the potential is periodic (and hence $f(z) = f(z+2L)$) because the series existing in the interval $(-L, L)$ undergoes periodicity and is true for all z . Hence the method should be useful for taking account of periodic potential such as that generated by an alternating double bond system in a polyene or the potential variation over identical atomic cores. The intrinsic symmetry of such situations brings about considerable simplifications in the algebra. In fact, the only requirement is that the function be analytic in each region.

Method 2. Use of a linear variation function

An approximation of the z -parts of the total wave functions in all the potential regions may be obtained by expressing them as linear combinations of the complete set of sine and cosine functions of the simple infinite well thus:

$$\psi_i = \frac{1}{\sqrt{L}} \sum_{n=1}^{\infty} a_{in} \cos (2n-1) \frac{\pi z}{2L} + b_{in} \sin \frac{2n \pi z}{2L} \quad (7)$$

When the well possesses infinite potential end walls then the above series vanishes at $-L$ and L but, when the walls are not infinite, we must impose a finite cut-off on the wave function at points outside them and assume it to be zero at these points. The same criteria in selecting such points as for method 1 will then operate.

Although the series is, in principle, an infinite one, in practice, if the exact wave functions exhibit sinusoidal behaviour over large regions of space then a few terms only of the series should suffice to simulate them.

If the series is expanded to k terms a Hamiltonian matrix of dimension $2k \times 2k$ may be constructed. This has diagonal and off-diagonal elements of the following form,

Diagonals — the $(2n-1)^{\text{th}}$ elements are,

$$\frac{1}{L} \left\langle \cos (2n-1) \frac{\pi z}{2L} \left| -\frac{1}{2} \frac{d^2}{dz^2} + \sum_{j=1}^l V_j \right| \cos (2n-1) \frac{\pi z}{2L} \right\rangle$$

the $2n^{\text{th}}$ elements are

$$\frac{1}{L} \left\langle \sin \frac{2n\pi z}{2L} \left| -\frac{1}{2} \frac{d^2}{dz^2} + \sum_{j=1}^l V_j \right| \sin \frac{2n\pi z}{2L} \right\rangle.$$

Off diagonals $m \neq n$.

The $[2n-1, 2m-1]^{\text{th}}$ elements are

$$\frac{1}{L} \left\langle \cos (2n-1) \frac{\pi z}{2L} \left| \sum_{j=1}^l V_j \right| \cos (2m-1) \frac{\pi z}{2L} \right\rangle$$

the $[2n, 2m]^{\text{th}}$ are,

$$\frac{1}{L} \left\langle \sin \frac{2n\pi z}{2L} \left| \sum_{j=1}^l V_j \right| \sin \frac{2m\pi z}{2L} \right\rangle$$

and the $(2n-1, 2n)^{\text{th}}$ are,

$$\frac{1}{L} \left\langle \cos (2n-1) \frac{\pi z}{2L} \left| \sum_{j=1}^l V_j \right| \sin \frac{2n\pi z}{2L} \right\rangle.$$

In all of the latter three cases the kinetic term in the operator vanishes by symmetry and the perturbing potential only mixes the levels. Furthermore, the matrix elements generated from the last expression are zero if the overall potential is symmetric about the origin. In calculating these matrix elements the potentials are integrated only across their local limits because they are step functions.

The Hamiltonian matrix is now diagonalised to yield its eigenvalues and normalised eigenvectors. The former are just the energies of the one-dimensional well perturbed by the introduction of subsidiary internal potential steps, whilst the latter determine the contribution of each separate sine or cosine function to the total linear combination. In the limit where all barriers have zero height and width and the end walls are infinite an element of each eigenvector corresponding to the appropriate simple well level is unity. Moreover when the overall potential is symmetric to inversion through the origin the constituent sine and cosine series do not mix and they describe the exact antisymmetric and symmetric wave functions respectively.

This technique has a number of advantages over both the exact and the Fourier approach to the problem,

a) No complex quantum conditions, such as are embodied in equations (3), and which are extremely difficult to generalise need be set up. The energies of the system are obtained automatically.

b) the evaluation of the troublesome normalisation constants A, B, C etc., which are required for the Fourier method, is obviated since the eigenvectors are always normalised to unity.

c) the complete set of wave functions for all levels is obtained simultaneously although those representing higher levels will be less accurate.

d) the potential chosen need not be a step function; indeed it can be any general one dimensional potential function. If it is then expressed as a Fourier series, the constituent integrals required for the matrix elements can be obtained exactly.

e) other forms of linear variation function may be used e.g. composed from the orthogonal set $(x+L)(x-L)^n$ in which n runs from 1 to any finite number of terms.

f) the method of evaluation of the electronic interaction integrals is similar (and simpler) than for the full Fourier series (*vide infra*) Interaction integrals.

In the execution of the *A.S.F.E. M.O.* method [1], [2] Coulomb and Exchange integrals arise of the form,

$$J_{pq} = \iint \psi_p(\mu) \psi_q(\nu) \frac{e^2}{r_{\mu\nu}} \psi_p(\mu) \psi_q(\nu) d\tau_\mu d\tau_\nu$$

and

$$K_{pq} = \iint \psi_p(\mu) \psi_q(\nu) \frac{e^2}{r_{\mu\nu}} \psi_q(\mu) \psi_p(\nu) d\tau_\mu d\tau_\nu$$

where ψ_p and ψ_q are free-electron molecular orbitals. Olszewski has developed an elegant technique for reducing and computing these integrals when ψ_p and ψ_q are simple sine functions [2]. The quantity $\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$ where \mathbf{r} and \mathbf{r}' are the vector distances of the μ^{th} and ν^{th}

electrons from the origin, is the Green's function (G) for the three dimensional Laplace-Poisson operator and hence satisfies the δ -function equation,

$$\nabla^2 G = -4\pi\delta(\mathbf{r}-\mathbf{r}') \quad (8)$$

The development of the Green's function will be deferred until the types of basic integrals to be evaluated are defined. If the general Fourier series is substituted into the above expression for J_{pq} then there results,

$$\begin{aligned} J_{pq} = & A^4 \int_L^{+L} \int_L^{+L} \int_0^R \int_0^R \int_0^{2\pi} \int_0^{2\pi} \left[\frac{1}{2} A_{0p} + \sum_{n=1}^{\infty} A_{np} \cos \frac{n\pi z}{L} + \right. \\ & \left. + B_{np} \sin \frac{n\pi z}{L} \right]^2 \times \\ & \times \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \left[\frac{1}{2} A_{0q} + \sum_{n=1}^{\infty} A_{nq} \frac{\cos n \pi z'}{L} + B_{nq} \sin \frac{n\pi z'}{L} \right]^2 \times \\ & \times J_1^2(kr) J_1^2(kr') \cos^2 \varphi \cos^2 \varphi' r dr r' dr' d\varphi d\varphi' dz dz' \end{aligned} \quad (9)$$

(A is the radial and angular normalisation constant.)

On multiplying out the summations 21 different types of integrals emerge. These are (writing G = Green's function, $c(n) = \cos \frac{n\pi z}{L}$, $c'(n) = \cos \frac{n\pi z'}{L}$, $s(n) = \sin \frac{n\pi z}{L}$, $s'(m) = \sin \frac{m\pi z'}{L}$ and leaving aside the Fourier coefficients and the angular and radial factors.

$$\begin{aligned} & \langle 1|G|1 \rangle, \langle 1|G|c'(n) c'(m) \rangle, \langle 1|G|s'(n) s'(m) \rangle, \\ & \langle 1|G|c'(n) \rangle, \langle 1|G|s'(n) \rangle, \langle 1|G|c'(n) s'(m) \rangle, \\ & \langle c(k) c(l)|G|c'(n) c'(m) \rangle, \langle c(k) c(l)|G|s'(m) s'(n) \rangle, \\ & \langle c(k) c(l)|G|c'(n) \rangle, \langle c(k) c(l)|G|s(n) \rangle, \langle c(k) c(l)|G|c'(n) s'(m) \rangle, \\ & \langle s(k) s(l)|G|s'(n) s'(m) \rangle, \langle s(k) s(l)|G|c'(n) \rangle, \langle s(k) s(l)|G|s'(n) \rangle, \\ & \langle s(k) s(l)|G|c'(n) s'(m) \rangle, \langle c(k)|G|c'(n) \rangle, \langle c(k)|G|s'(n) \rangle, \langle c(k)|G|c'(n) s'(m) \rangle, \\ & \langle s(k)|G|s'(n) \rangle, \langle s(k)|G|c'(n) s'(m) \rangle, \langle c(k) ss(l)|G|c'(n) s'(m) \rangle. \end{aligned}$$

These are all reducible to six basic integral forms and an expression for J_{pq} incorporating the latter integrals is given in the Appendix.

When the problem has symmetry, *e. g.* if there are a set of eigenfunctions which are alternately symmetric and antisymmetric to inversion, then the above 21 integrals reduce to nine for J_{pq} with symmetry of ψ_p and ψ_q different and to six when ψ_p and ψ_q have the same symmetry. The exchange integrals K_{pq} yield, on expansion, an identical set of integrals to the above. However, the combinations of Fourier coefficients differ which confers a different numerical value for given p and q .

Application to the calculation of the electronic states of divinylborane

The method was tested by applying it to the calculation of the electronic states and spectrum of divinylborane. This is a convenient system for study as (a) the experimental spectrum is well characterized and (b) the electronic states have previously been calculated by a version of the A.S.F.E.M.O. method [4]. In the latter the core eigenenergies were obtained exactly by solution of the barrier problem whereas the electronic interaction integrals were computed with neglect of the central barrier representing boron. A potential of the form of $l(a)$ was used — the height of the central barrier was 11.22 eV and the end walls 30eV [4]. In the calculation of excited states configuration interaction between all the singlet and triplet A_1 and B_1 states was included.

The results of the present treatment are given in the following table together with comparable figures from ref. [4].

TABLE
Electronic States of Divinylmethylborane (eV)

	Present work	Ref. [4]	Experimental Energy Ref. [4]
E_1	1.789	1.741	—
E_2	1.907	1.891	—
E_3	6.723	6.653	—
E_4	7.576	7.469	—
$V_{23}(^1B_1)$	5.27	6.22	5.58
$T_{23}(^3B_1)$	4.89	5.00	—
$V_{13}(^1A_1)$	6.11	6.08	6.19
$T_{13}(^3A_1)$	5.52	5.74	—
$V_{14}(^1B_1)$	7.49	7.65	—
$T_{14}(^3B_1)$	7.42	7.59	—
$V_{24}(^1A_1)$	7.83	7.04	—
$T_{24}(^3A_1)$	7.64	6.84	—

It can immediately be seen that the agreement between the energy calculated for the lowest singlet state (1B_1) and the experimental band energy is better than that previously obtained from the A.S.F.E.M.O. calculation which neglected the central potential barrier. For the second (1A_1) state of the molecule the agreement with experiment is also improved, although less markedly. We may thus conclude that the method developed here will yield good results for free-electron systems containing potential wells or barrier. The improvement in estimation of the interaction integrals over the simple well will become more marked with increasing height and width and number of potential steps. An investigation of the effects of these factors will be presented at a later date.

Evaluation of the basic integrals

The work of Olszewski deals with the evaluation of those integrals in which $f(z)$, $f(z')$ are either constant or involve only cosine products. The integrals were developed in three

dimensional cylindrical coordinates and finally, so as to render the problem numerically tractable, the radius of the cylinder was allowed to tend to the limit of zero. This reduces the problem to a single dimension. It is reasonable to apply the latter limiting process since the radial motions of the electrons will normally remain in their ground states and low energy excitations will be achieved most readily along the chain. However, the three dimensional model must be retained for some purposes *e. g.* one of the deficiencies of free electron theory is that, in one dimension, the transition moments of electronic excitations polarised at right angles to the molecular chain cannot be predicted. Hence if it is desired to extend the model to include this feature, or vibronic coupling, then two or three dimensions become mandatory to describe the true geometry of the molecule.

A number of other basic integrals, not specified in the previous work, arise from the present generalisations. The reduction of a typical case $\langle s(n) | G | s'(m) \rangle$ is given below and, in the appendix, formulae for the remainder are quoted. It is convenient to let $a = \frac{n\pi}{L}$ and $c = \frac{m\pi}{L}$ in carrying through the analysis.

The δ -function, $\delta(\mathbf{r}-\mathbf{r}')$ is expressible in cylindrical coordinates and is, [2].

$$G = \delta(\mathbf{r}-\mathbf{r}') = \frac{1}{r} \delta(r-r') \delta(z-z') \delta(\varphi-\varphi') \quad (10)$$

$$G = \frac{1}{2\pi} \int_0^{\infty} \int_{-\infty}^{+\infty} \frac{e^{i\kappa|z-z'|}}{\kappa^2+k^2} d\kappa k J_0(kr) J_0(kr') dk \times \delta(\varphi-\varphi'). \quad (11)$$

This integral representation is uniformly convergent over the whole z, z' region and this fact allows the order of integration to be reversed at will.

Substitution of this expression for G in $\langle s(a) | G | s'(c) \rangle$ and immediate integration over the angle s yields,

$$I = \frac{3e^{24}}{2\pi R^4} \int_0^R dr \int_0^R dr' \int_{-L}^{+L} dz \int_{-L}^{+L} dz' \sin az \sin cz' \int_{-\infty}^{+\infty} d\kappa \int_0^{\infty} dk \times \\ \times \frac{e^{i\kappa|z-z'|}}{\kappa^2+k^2} k J_0(kr) J_0(kr') rr'. \quad (12)$$

(the angular and radial factors are included in this expression)

The infinite integral over κ may be transformed into a contour integral because the function $\frac{e^{i\kappa|z-z'|}}{\kappa^2+k^2}$ has simple poles lying on the imaginary axis at $\pm ik$ and hence the function may be expanded in a Laurent series around these poles. The appropriate closed integration contours which avoid the poles are the infinite semicircles based on the axis from $-\infty$ to $+\infty$ and the upper complex half plane in which the pole at ik lies. In the limit $R \rightarrow \infty$ the

contribution around the infinite semicircle vanishes and hence by Cauchy's Theorem,

$\int_{-\infty}^{+\infty} \frac{e^{ix|z-z'|}}{\kappa^2+k^2} dk = 2\pi i$ (sum of the residues at the poles). The residue at ik is the first negative coefficient in the Laurent expansion and is given by

$$\lim_{\kappa \rightarrow ik} \frac{e^{ix|z-z'|} (\kappa - ik)}{(\kappa + ik) (\kappa - ik)^2} \quad (13)$$

Thus the infinite integral over κ becomes equal to

$$\frac{e^{-k|z-z'|}}{k}.$$

We may now integrate over z and z' between the limits $\pm L$, taking account of the modulus sign on their difference and this yields,

$$I = \frac{3e^{24}}{2R^4} \int_0^R dr \int_0^R dr' \int_0^\infty dk \frac{2ac \cos aL \cos cL}{(a^2+k^2)(c^2+k^2)} (1-e^{-2kL}) \times J_0(kr) J_0(kr'). \quad (14)$$

In deriving the above, $\sin aL$ and $\sin cL$ both vanish as $cL = m\pi$ and $aL = n\pi$.

The product of the zero order Bessel functions in the variables r, r' has the following integral representation [6].

$$J_0(kr) J_0(kr') = \frac{1}{\pi} \int_0^\pi J_0(k\psi) d\gamma \quad (15)$$

where

$$\psi = (r^2 + r'^2 - 2r' \cos \gamma)^{\frac{1}{2}}. \quad (16)$$

Hence

$$I = \frac{3e^{24}}{2R^4} \frac{2ac \cos aL \cos cL}{\pi (c^2 - a^2)} \left[\int_0^\pi d\gamma \int_0^\infty dk \left\{ \frac{1}{(a^2+k^2)} - \frac{1}{(c^2+k^2)} - \frac{e^{-2kL}}{(a^2+k^2)} + \frac{e^{-2kL}}{(c^2+k^2)} \right\} J_0(k\psi) \right]. \quad (17)$$

The integrals over k of the type

$$\int_0^\infty \frac{e^{-2Lk} J_0(k\psi)}{(c^2+k^2)} dk$$

may be evaluated by primary expansion of $J_0(k\psi)$ in a series and term by term integration. Each separate integral is then in standard form [7] thus,

$$\int_0^{\infty} \frac{e^{-2Lk} J_0(k\psi) dk}{(c^2+k^2)} = \frac{-1}{C} I_0(\psi c) (\text{Si}(2cL) \cos 2cL) + K(\psi c) \quad (18)$$

where $I_\nu(z) = \sum_{n=0}^{\infty} \frac{(Z/2)^{\nu+2n}}{n! \Gamma(\nu+m+1)}$ *i. e.* the Hankel function of imaginary argument and

$$K(\psi c) = \sum_{n=1}^{\infty} \sum_{k=1}^n \frac{(-1)^n}{(n!)^2} \frac{1}{L^{2n-1}} (2n-2k)! \left(\frac{\psi}{2}\right)^{2n} (-c^2 L^2)^{k-1}.$$

By a similar procedure the second type of integral *i. e.*

$$\int_0^{\infty} \frac{J_0(k\psi)}{(c^2+k^2)} dk,$$

becomes equal to,

$$\frac{\pi}{2c} (I_0(\psi c) - L_0(\psi c))$$

where L_0 is the zero order Struve function of imaginary argument defined by

$$L_\nu(z) = \sum_{m=0}^{\infty} \frac{(z/2)^{(\nu+2m+1)}}{\Gamma(m+3/2)\Gamma(\nu+m+3/2)}.$$

Inserting these expressions in (17) we get

$$\begin{aligned} I = & \frac{3e^2 4.2ac \cos aL \cos cL}{2R^4 \pi (c^2 - a^2)} \left[\frac{\pi}{2a} \left(I_0(\psi a) - L_0(\psi a) \right) - \frac{\pi}{2c} \left(I_0(\psi c) - \right. \right. \\ & \left. \left. - L_0(\psi c) \right) - \left(\frac{1}{a} I_0(\psi a) (-\text{Si}(2aL) \cos 2aL) + K(\psi a) \right) + \right. \\ & \left. + \left(\frac{1}{c} I_0(\psi c) (-\text{Si}(2cL) \cos 2cL) + K(\psi c) \right) \right]. \quad (19) \end{aligned}$$

Now ψ may itself be developed in an absolutely convergent infinite series in ascending powers of r'/r ($r > r'$) *i. e.*

$$\psi = r \sum_{m=0}^{\infty} A_m^{-1} (\cos \gamma) \frac{(r')^m}{r}. \quad (20)$$

The expansion coefficients A_m^{-1} derive from Gegenbauer's generalisation of Neumann's polynomial and are,

$$A_n^{\nu}(t) = \frac{2^{\nu+n}(\nu+n)}{t^{n+1}} \sum_{m=0}^{\leq \frac{1}{2}n} \frac{\Gamma(\nu+n-m)}{m!} (t/2)^{2m} \quad (21)$$

which is valid for negative, non-integral ν in our case $\nu = -\frac{1}{2}$ and $t = \cos \gamma$.

It is now straightforward to integrate directly over r, r' and γ following which R is allowed to tend to zero. Bearing in mind that the normalisation factor for the radial part of the total function (equation (19)) is proportional to $1/R^4$ the effect of these operations is to remove the series $K(\psi a), K(\psi c), L_0(\psi a)$ and $L_0(\psi c)$. This is because all terms in the integrated form of these series are proportional to higher powers of R than R^4 . The leading terms only of $I_0(\psi a)$ and $I_0(\psi c)$ (*i. e.* $(\psi a/2)^0$ and $(\psi c/2)^0$) survive but because of the zero exponent all the Gegenbauer coefficients are inoperative. Hence the integration over γ yields merely a multiplicative factor π . The final result is,

$$I = 3e^2 \cos aL \cos cL \frac{(c\text{Si}(2aL) - a\text{Si}(2cL))}{(c^2 - a^2)} \quad (22)$$

where

$$\text{Si}(x) = \text{si}(x) + \pi/2.$$

Now $aL = n\pi$ and $cL = m\pi$ and so

$$\frac{4e^2}{R^4 \pi^2} \langle s(n) | G | s'(m) \rangle = \frac{3e^2 (-1)^{n+m} L}{\pi} \left[\frac{m \text{Si}(2n\pi) - n \text{Si}(2m\pi)}{(m^2 - n^2)} \right]. \quad (23)$$

Alternatively if R does not tend to zero we may obtain the full expression for the three-dimensional interaction integrals. The ease of evaluation of these integrals will depend largely on the rapidity of convergence of the constituent series.

APPENDIX

1. Fourier series

For a one dimensional linear well with infinite walls and a central potential barrier (Fig. 1d) there are a set of wave functions which alternate in symmetry. Numbers 1, 3, 5 ... $2n-1$, are symmetric to inversion hence only the cosine half-series is required to represent them. They are, moreover, bounded at $\pm L$ by the infinite walls. The Fourier series for these symmetric levels is thus simply the sum of the separate series over each region, *i. e.*

$$f(z) \approx (A/L\alpha) \{ \sin \alpha L (\sin \alpha L - \sin \alpha a) + \cos \alpha L (\cos \alpha L - \cos \alpha a) \} + B(e^{\beta a} - 1)/L\beta + \\ + \sum_{n=1}^{\infty} \left[A/L \left[\sin \alpha L \left\{ \frac{\sin \alpha L (-1)^n - \sin \alpha a \cos n\pi a/L - \cos \alpha a \sin n\pi a/L}{\alpha + n\pi/L} \right. \right. \right. \\ \left. \left. \left. + \frac{\sin \alpha L (-1)^n - \sin \alpha a \cos n\pi a/L + \cos \alpha a \sin n\pi a/L}{\alpha - n\pi/L} \right\} \right] \right]$$

$$\begin{aligned}
& + \cos \alpha L \left\{ \frac{\cos \alpha L (-1)^n - \cos \alpha a \cos n\pi a/L + \sin \alpha a \sin n\pi a/L}{\alpha + n\pi/L} + \right. \\
& \left. + \frac{\cos \alpha L (-1)^n - \cos \alpha a \cos n\pi a/L - \sin \alpha a \sin n\pi a/L}{\alpha - n\pi/L} \right\} + \\
& \left. + \frac{2Be^{\beta a}(\beta \cos n\pi a/L + n\pi/L \sin n\pi a/L - \beta)}{L(\beta^2 + n^2\pi^2/L^2)} \right] \times \cos n\pi z/L. \quad (24)
\end{aligned}$$

In this expression α , β , L and a have the same significance as in equations (3).

This type of equation is readily set up for computation and n may be taken as large as we please subject to approximation to $f(z)$ in the mean, *i. e.* the relative error is given by

$$\int_{-L}^{+L} [f(z) - \sum_{r=1}^n A_r \varphi_r]^2 dz. \quad (25)$$

The same series is appropriate for any periodic extension of the potential.

2. Expansion of the Coulomb Integral J_{pq} between F.E.M.O's p and q

We assume that the wave functions have no symmetry and hence the total Fourier series is required. The introduction of symmetry will reduce the following expression considerably. We have

$$\begin{aligned}
\psi_p(x) &= \frac{1}{2} A_{0p} + \sum_{n=1}^{\infty} A_{np} \cos \frac{n\pi x}{L} + B_{np} \sin \frac{n\pi x}{L} \\
\psi_q(z) &= \frac{1}{2} A_{0q} + \sum_{n=1}^{\infty} A_{nq} \cos \frac{n\pi z}{L} + B_{nq} \sin \frac{n\pi z}{L}.
\end{aligned}$$

If these expressions, together with the appropriate radial and angular normalising factors (A) are substituted into (9), and writing

$$\langle 1|1 \rangle = C_{0,0}, \quad \langle 1|c'(n) \rangle = C_{0,n}$$

$$\langle c(k)|c'(n) \rangle = C_{k,n} \text{ and } \langle s(k)|s'(n) \rangle = S_{k,n}$$

(basic integrals of the type $\langle 1|s'(n) \rangle$ and $\langle s(k)|c'(n) \rangle$ vanish) then we have the following equation for J_{pq}

$$\begin{aligned}
J_{pq} &= \left(\frac{1}{16} A_{0p}^2 A_{0q}^2 C_{0,0} + \frac{1}{8} A_{0q}^2 A_{0p} \left[\sum_n A_{np} C_{0,n} + \sum_m A_{mp} C_{0,m} \right] + \frac{1}{8} A_{0p} A_{0q}^2 \times \right. \\
&\times \sum_k A_{kq} C_{0,k} + \sum_l A_{lp} C_{0,l} + \frac{1}{8} A_{0q}^2 \left[\sum_n \sum_m \{ A_{np} A_{mp} (C_{0,n+m} + C_{0,n-m}) + \right. \\
&\left. + B_{np} B_{mp} (C_{0,n-m} - C_{0,n+m}) \} \right] + \frac{1}{4} A_{0q} A_{0p} \left[\sum_n \sum_k \{ A_{np} \times A_{kq} C_{n,k} + B_{np} B_{kq} S_{n,k} \} \right]
\end{aligned}$$

$$\begin{aligned}
& + \sum_m \sum_k \{A_{mp}A_{kq}C_{m,k} + B_{mp}B_{kq}S_{m,k}\} + \sum_n \sum_l \{A_{np}A_{lq}C_{n,l} + B_{np}B_{lq}S_{n,l}\} \\
& + \sum_n \sum_l \{A_{mp}A_{lq}C_{m,l} + B_{mp}B_{lq}S_{m,l}\} + \frac{1}{4} A_{0q} \left[\sum_n \sum_m \sum_k \{A_{np}A_{mp}A_{kq}(C_{k,n+m} + C_{k,n-m} \right. \\
& + B_{np}B_{mp}A_{kq}(C_{k,n-m} - C_{k,n+m}) + A_{mp}A_{np}B_{kq}(S_{k,n+m} + S_{k,n-m}) + A_{np}B_{mp}B_{kq}(S_{k,m+n} \\
& + S_{k,m-n})\} + \sum_n \sum_m \sum_l \{A_{np}A_{mp}A_{lq}(C_{l,n+m} + C_{l,n-m}) + B_{np}B_{mp}A_{lq}(C_{l,n-m} - C_{l,n+m}) \\
& + A_{np}B_{mp}B_{lq}(S_{l,n+m} + S_{l,n-m}) + A_{mp}B_{np}B_{lq}(S_{l,m+n} + S_{l,m-n})\} \\
& + \frac{1}{8} A_{0p}^2 \left[\sum_k \sum_l \{A_{kq}A_{lq}(C_{0,k+l} + C_{0,k-l}) + B_{kq}B_{lq}(C_{0,k-l} - C_{0,k+l}) \right. \\
& + \frac{1}{4} A_{0p} \left[\sum_n \sum_k \sum_l \{A_{np}A_{kq}A_{lq}(C_{n,k+l} + C_{n,k-l}) + B_{np}A_{lq}B_{kq}(S_{n,l+k} + S_{n,l-k}) \right. \\
& + B_{np}A_{kq}B_{lq}(S_{n,k+l} + S_{n,k-l}) + A_{np}B_{kq}B_{lq}(C_{n,k-l} - C_{n,k+l})\} \\
& + \sum_m \sum_k \sum_l \{A_{mp}A_{kq}A_{lq}(C_{m,k+l} + C_{m,k-l}) + B_{mp}A_{lq}B_{kq}(S_{m,l+k} + S_{m,l-k}) \\
& + B_{mp}A_{kq}B_{lq}(S_{m,k+l} + S_{m,k-l}) + A_{mp}B_{kq}B_{lq}(C_{m,k-l} - C_{m,k+l})\} \left. \right] + \frac{1}{4} \times \\
& \times \left[\sum_n \sum_m \sum_k \sum_l \{A_{np}A_{mp}A_{kq}A_{lq}(C_{n+m,k+l} + C_{n-m,k-l} + C_{n+m,k-l} + C_{n+m,k-l}) \right. \\
& + B_{np}B_{mp}A_{kq}A_{lq}(C_{n-m,k+l} + C_{n-m,k-l} - C_{n+m,k+l} - C_{n+m,k-l}) + A_{mp}B_{np}A_{lq}B_{kq} \times \\
& \times (S_{n+m,k+l} + S_{n+m,k-l} + S_{n-m,k+l} + S_{n-m,k-l}) + A_{np}B_{mp}A_{lq}B_{kq}(S_{m+n,k+l} + \\
& + S_{m+n,k-l} + S_{m-n,k+l} + S_{m-n,k-l}) + A_{mp}B_{np}A_{kq}B_{lq}(S_{n+m,l+k} + S_{n+m,l-k} + \\
& + S_{n-m,l+k} + S_{n-m,l-k}) + A_{np}B_{mp}A_{kq}B_{lq}(S_{m-n,l+k} + S_{n+m,l-k} + S_{n-m,l+k} + S_{n-m,l-k}) + \\
& + A_{np}A_{mp}B_{kq}B_{lq}(C_{n+m,k-l} + C_{n-m,k-l} - C_{n+m,k+l} - C_{n-m,k+l}) + B_{np}B_{mp}B_{kq}B_{lq} \times \\
& \left. \left. \times (C_{n+m,k-l} + C_{n+m,k+l} - C_{n+m,k-l} - C_{n-m,k+l})\right\} \right] \times e^2 A^4 \quad (26)
\end{aligned}$$

This expression simplifies considerably when the system has some symmetry and, furthermore, the suffixes n , m , k , l will generally have only a limited range of values. A similar expression may be derived to compute J_{pq} for the linear variation functions. This is considerably simpler because the leading constant term which appears in the Fourier series is absent.

3. Formulae for basic interaction integrals

The following derive from the limit of $R \rightarrow 0$ imposed on the three dimensional interaction integral. The angular and radial normalisation constants are therefore included.

$$(i) \quad \langle c(n) | c'(m) \rangle = \frac{3(-1)^{n+m} e^2 L}{\pi} \left[\frac{n \operatorname{Si}(2n\pi) - m \operatorname{Si}(2m\pi)}{(m^2 - n^2)} \right] \quad n \neq m$$

$$= \frac{-3Le^2}{2\pi n} \operatorname{Si}(2n\pi) \quad n = m$$

$$(ii) \quad \langle 1 | c'(n) \rangle = \frac{3(-1)^{n+1} e^2 L}{\pi n} \operatorname{Si}(2n\pi)$$

$$(iii) \quad \langle 1 | 1 \rangle = -3e^2 L$$

$$(iv) \quad \langle s(n) | s'(m) \rangle = \frac{3(-1)^{n+m} e^2 L}{\pi} \left[\frac{m \operatorname{Si}(2n\pi) - n \operatorname{Si}(2m\pi)}{(m^2 - n^2)} \right] \quad n \neq m$$

$$= \frac{3Le^2}{2n\pi} \operatorname{Si}(2n\pi) \quad n = m$$

$$v) \quad \langle 1 | s'(n) \rangle = 0$$

$$(vi) \quad \langle s(n) | c'(m) \rangle = 0.$$

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