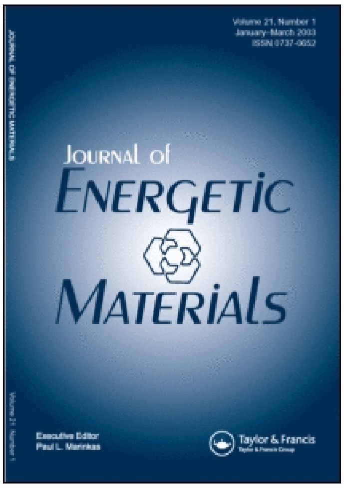

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ON THE APPLICATION OF BOUNDARY PERTURBATION THEORY FOR MODELLING THE EFFECT OF HIGH PRESSURE ON SIMPLE CHEMICAL SYSTEMS

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ABSTRACT

The effects of high pressure on a quantum system may be described by introducing an external wall potential which represents the interaction with neighbouring atoms and molecules. Here we present a generalisation of the Hull and Julius[1] boundary perturbation method of solving the Schrodinger equation for an enclosed system. For the one-dimensional case our method gives the exact solution. The method may be also applied to any separable multidimensional Schrodinger equation. Applications to the simple systems: H_2^+, and He, are discussed.

INTRODUCTION

It is well known that the standard methods of theoretical quantum chemistry describe the states of atoms and molecules at zero pressure. There is experimental evidence that the properties of atoms and molecules at high pressure are very different from those at zero pressure. Therefore, to model the reactions occurring in detonations, where the pressure can easily exceed 100 kbar, it is necessary to include the effect of pressure in the quantum calculations.

From the microscopic point of view pressure appears as a result of the mutual interactions of atoms in the system and all that is necessary to model the effect of pressure on a single molecule is to take these interactions into account. In some special cases, as for example in crystaline solids, the high symmetry simplifies the problem and makes the calculations possible. But during detonations the interactions of a given molecule with its neighbours seems to be random. Of course it is possible, at least in principle to perform quantum all-electron computations for a molecule and a chosen configuration of its neighbours, but the information we obtain will be very limited because the result will be strongly dependent on the configuration chosen.

Therefore it seems worthwile to study simple models describing the influence of pressure on quantum systems. For example, we can consider a model of a system in a box; within this box the hamiltonian is the same as for zero pressure, outside it a model potential approximates all the interaction with neighbouring atoms. This idea recalls the methods of solid state physics, where the properties of a crystal can be studied by considering a single units cell. The simplest choice for the model potential is a potential wall. The idea of simulating the effect of pressure on an atom by enclosing it in a spherical box and replacing the interaction with neighbouring particles by a wall potential was first introduced by Michels, De Boor and Bijl in 1937[2]. Most of the papers published since this pioneering work[3-11] have been concerned with the infinite potential wall because this model leads to the "nice" mathematical condition that the wave function vanishes at the boundary of the box. The wave function of a system enclosed in a box with infinite walls is localized within the box and it corresponds well to a general sense that a system under pressure is more concentrated than when the pressure is zero. Calculations have been performed for a few light atoms[5,6] and for the hydrogen molecule[7] and hydrogen molecular ion[7,10,12,13]. For testing the accuracy of box models it is important that the change of total electronic kinetic energy of a gas caused by pressure can be obtained from the equation of state[2]. The qualitative behaviour of electronic kinetic energy as a function of pressure predicted by the infinite potential wall model is in agreement with observation but the quantitative comparison fails because the hard box model overestimates by a few times the effect of pressure. This can be easily understood as the rapid increase of the curvature of the wave function is a consequence of two assumptions: normalization within the box and the boundary condition which sets the wave function to zero at the boundary.

The infinite wall potential model in its original version cannot be improved as the only parameter involved is the radius of the box which determines the pressure and there are no further adjustable parameters. However Michels's idea can be simply generalized if we consider the box with a finite potential wall U_0 instead of an infinite one (such an idea was suggested by many authors, see reference 7 for example). This approach seems to be more realistic because the potential of the interaction of an electron with the neighbouring atoms is far from being infinite and the wave function must extend over neighbouring atoms.

From the mathematical point of view, the infinite potential corresponds to the Dirichlet boundary conditions, whereas if the potential wall is finite the Neumann boundary conditions are satisfied. Unfortunately the direct solution of the Schrodinger equation for an external wall potential is usually more difficult than for the free unenclosed system. Here we present a method which simplifies this problem and, for one dimensional systems, gives the exact energy and wave function. We also discuss the applications of our method for modelling simple chemical systems under high pressure.

THE BOUNDARY PERTURBATION THEORY

The boundary perturbation theory can be regarded as a "lazy man's approach" to the problem of solving the Schrodinger equation with additional boundary conditions. It is based on the assumption that the knowledge of the energy E_0 and the wave function Φ_0 of the unenclosed system provide us with the information which allows one to calculate the energy of the enclosed system with arbitrary boundary conditions without solving the Schrodinger equation. The first step in this direction was taken by Hull and Julius[1], who proposed the following expression to calculate the difference of energy ΔE between enclosed (hard box) and unenclosed system described by a simple one-dimensional Schrodinger equation,

$$\Delta E = \left(2 \int_{c}^{R} \Phi_0^{-2}(x)dx\right)^{-1} \tag{1}$$

where R denotes the position of the boundary.

Formula (1) is asymptotic and Hull and Julius do not specify the lower limit c of the integral. It has been used to study the effect of pressure on the hydrogen atom[1] and on the H_2^+ ion[12]. The qualitative behaviour of energy as a function of pressure is represented correctly, but comparison of the results given by the Hull and Julius method with the exact solution of the Schrodinger equation or with more accurate variational calculations shows that formula (1) becomes very inaccurate at high pressures.

Let us consider the system, which at zero pressure is described by the Schrodinger equation

$$-\frac{1}{2}\sum_i{}' \frac{\partial^2}{\partial x_i^2}\Phi_0 + V\Phi_0 = E_0\Phi_0 \tag{2}$$

where V denotes the full potential. According to our model of pressure the potential inside the box remains the same on enclosing system. Therefore the Schrodinger equation inside the box Ω is

$$-\frac{1}{2}\sum_i \frac{\partial^2}{\partial x_i{}^2}\Phi(x) + V\Phi(x) = E\Phi(x) \qquad x \in \Omega \qquad (3)$$

Another Schrödinger equation of the form (3), which contains the model potential describes the wave function of enclosed system Φ outside the box. Now let us assume that there exists a nonsingular function f which relates Φ and Φ_0, namely:

$$\Phi(x) = f(x)\Phi_0(x) \qquad x \in \Omega. \qquad (4)$$

This assumption is very strong[14], however for a small system we will discuss later if it does not lead to any limitations of the method. It is easy to notice that when we multiply equations (2) and (3) by Φ and Φ_0 respectively and the subtract one from the other we get the following equation

$$-\frac{1}{2}\sum_i \frac{\partial}{\partial x_i}\left(\Phi_0{}^2 \frac{\partial}{\partial x_i} f\right) = (E-E_0)\,\Phi_0{}^2\, f = \Delta E\Phi_0{}^2 f \qquad x \in \Omega \qquad (5)$$

where the boundary conditions for function f are connected with the potential outside the box. Equation (5) is equivalent to (3) when condition (4) is satisfied, but does not involve the potential V because the function Φ_0 contains all the necessary information about it. This makes equation (5) a good starting point for a boundary perturbation method. Unfortunately we do not know any general method of solving the multidimensional equations of the form (5) with arbitrary boundary conditions. In the following we present a method which works in the one-dimensional case for both the Dirichlet and Neumann boundary conditions and discuss its applications for modeling the effect of pressure.

Let us consider a general one-dimensional Schrodinger equation of the form

$$-\frac{1}{2}\frac{1}{h(x)}\frac{d}{dx}\left[g(x)\frac{d}{dx}\Phi_0(x)\right] + \qquad (6)$$

$$[V(x) - G(x)H(E_0) - A(E_0)]\,\Phi_0(x) = 0 \qquad x \in R$$

The functions $h(x)$, $g(x)$, $G(x)$, $H(E_0)$ and $A(E_0)$ are introduced in order to make the method more general; they can appear when equation (6) is obtained as a result of separation of the variables of a multidimensional Schrodinger equation. Now the equation corresponding to (5) reads

$$\frac{d}{dx}\left[g(x)\,\Phi_0^2(x)\,\frac{df}{dx}\right] = -2h(x)\,\{G(x)\,[H(E)-H(E_0)] +$$

$$A(E) - A(E_0)]\}\,f(x)\,\Phi_0^2(x) \qquad (7)$$

Let us assume that there exists $x_0 \in \Omega$ such that $g(x_0)\Phi_0^2(x_0)$ $f'(x_0) = 0$ (this assumption is only technical and it simplifies the final result, however it is satisfied for all they sytems discussed later). The differential equation (7) can be easily transformed to the following integral form

$$f(x) - f(R) = 2 \int_{x}^{R} ds\, g^{-1}(s)\, \Phi_0^{-2}(s) *$$

$$\int_{x_0}^{s} d\, th(t)\, \Phi_0^{2}(t)\, f(t)\, \{G(t)[H(E) - H(E_0)] + A(E) - A(E_0)\} \quad (8)$$

When we consider R as a boundary of the system, where the function Φ satisfies the condition

$$\Phi(R) + \gamma\, \Phi'(R) = 0 \qquad (9)$$

(for the infinite wall potential $\gamma = 0$) then equation (8) can be rewritten in the form

$$f(x) = \frac{2\gamma}{g(R)\Phi_0(R)(\gamma\Phi_0'(R) + \Phi_0(R))} \int_{x_0}^{R} dt\, f(t)\, \Phi_0^{2}(t) h(t) *$$

$$\{G(t)[H(E) - H(E_0)] + A(E) - A(E_0)\} +$$

$$2 \int_{x_0}^{R} dt\, f(t)\Phi_0^{2}(t) h(t) \{G(t)[H(E) - H(E_0)] + A(E) - A(E_0)\} *$$

$$\int_{\max(x,t)}^{R} ds\, \Phi_0^{-2}(s) g^{-1}(s) \qquad (10)$$

The integral equation (10) can be easily transformed to the matrix equation when the outer integral is approximated by a finite sum (for example by using Gaussian quadrature). Its solutions form a one-dimensional vector space and therefore E can be found as a zero of the main determinant of this equation. Equation (10) may be also used as a basis for an iterative algorithm[14]. The ground state of an enclosed system may be approached if we assume that in the first approximation $f^{(0)} \equiv 1$ and then continue using (10). To ensure the convergence to a specific element of the vector space of solutions of (10) another arbitrary condition for the function f is necessary (for example in the form $f(x_0) = 1$). It is worth noticing[14] that in the first approximation for the simplest case ($g \equiv h \equiv 1$, $A(E)=E$, $G \equiv 0$) the difference in energy between the unenclosed system and the system enclosed in hard box ($\gamma = 0$) is given by the Hull and Julius formula (1).

APPLICATION OF THE BOUNDARY PERTURBATION METHOD FOR SIMPLE SYSTEMS UNDER PRESSURE

Let us consider the hydrogen atom enclosed in a sphere of radius R. Let us assume that the potential outside this sphere is uniform and is equal to U_0. The Schrodinger equation for the ground state of this enclosed system reads

$$-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\Phi\right) - \left\{-\frac{\chi_{[0,R]}(r)}{r} + U_0(1-\chi_{[0,R]}(r)) - E\right\}\Phi = 0 \qquad (11)$$

where $\chi_{[0,R]}$ is the characteristic function of the interval $[0,R]$. The general equation (6) reduces to (11) when $h(r)=g(r)=r^2$, $G \equiv 0$, $A(E)=E$ and $x_0=0$. The solution of (11) outside the box is well known[17] and can be written

$$\Phi(r) = \frac{c}{r} \exp(-\sqrt{2(U_0-E)}\,(r-R)), \quad r \geqslant R, c=\text{const}. \tag{12}$$

It leads to the boundary condition in the form (9) where

$$\gamma = \frac{1}{R^{-1} + \sqrt{2(U_0-E)}} \tag{13}$$

When we take the wave function of the ground state of a free hydrogen atom as Φ_0 equation (10) can be easily solved numerically. The results for the energy of the enclosed hydrogen atom are presented in table 1. We compared our calculations with the exact solution of equation (10)[8] and both methods give the same energy.

TABLE 1

The energy (Rydberg units) of the ground state of the hydrogen atom enclosed in a spherical box of radius R (bohrs). U_0 = potential wall, E^{BPT} = energy obtianed from equation (10), E = exact result[8]

R	U_0	E^{BPT}	E
4.08671	∞	-.9707	-.9707
3.04187	∞	-.85734	-.8573
2.00000	∞	-.2500	-.2500
1.71208	∞	.2500	.2500
3.57457	1.	-.9803	-.9803
2.46766	1.	-.8900	-.8900
1.7221	1.	-.6400	-.6400
1.2513	1.	-.2066	-.2066

The same method as presented above for the hydrogen atom can be applied to helium. Within the self-consistent field method the ground state of the helium atom is described by a one-dimensional Schrodinger equation. When we neglect electron-electron correlations the wave function of the helium atom in its ground state is

$$\psi(\bar{r}_1,\bar{r}_2) = \phi(r_1)\phi(r_2)/4\pi \tag{14}$$

The Hartree-Fock equation for the orbital function ϕ of the helium atom enclosed in a sphere of radius R reads

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\phi\right) + 2(\epsilon - U(r))\phi = 0 \tag{15}$$

where

$$U(r) = \begin{cases} U_0 & r \geq R \\ U_0 - \frac{2}{r} + \frac{1}{4\pi}\int_{0\leq r_1\leq R} \frac{\phi^2(r_1)}{|\bar{r} - \bar{r}_1|}\, d\bar{r}_1 & r \leq R \end{cases}$$

and ϵ is the orbital energy. The boundary perturbation method cannot be directly applied to solve equation (15) because the electron-electron repulsion in the potential U(r) depends on the radius of the box as it involves the orbital function ϕ. Therefore the boundary perturbation method gives the solution (ϵ_B,ϕ_B) not of equation (15) but of the closely related equation

$$-\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\phi_B\right) + 2\left[\epsilon_B - \frac{2}{r} + \frac{1}{4\pi}\int_{0\leq r_1\leq\infty} d\bar{r}_1 \frac{\phi_0^2(r_1)}{|\bar{r} - \bar{r}_1|}\right]\phi_B = 0 \tag{16}$$

where ϕ_0 is the ground state orbital for the free atom. It can be easily shown that the change of total energy is

$$\Delta E = 2(\epsilon_B - \epsilon_0) + F(\phi - \phi_0) \tag{17}$$

where the functional F depends on terms of second and higher order in $\Phi-\Phi_0$. For large R, where the difference between Φ and Φ_0 is small, the last term in (17) can be neglected and the boundary perturbation method should give an accurate approximation to the direct solution of the Hartree-Fock equation (15). The results are compared with the total energy obtained by a direct solution of equation (15) (see Table 2). The difference between the Hartree-Fock energy for helium and that obtained from equation (10) does not exceed 2% for pressures up to 1 Mbar.

TABLE 2

The change of the total Hartree-Fock energy as a function of the box radius R and the wall potential U_0: ΔE_{SCF} - direct solution of the Hartree-Fock equation[15], ΔE_{BPT} - boundary perturbation method (all values except pressure in atomic units).

R	U_0	P/atom	ΔE_{SCF}	ΔE_{BPT}
3.2	-.2	4.0 10^3	.000543	.000543
3.2	-.1	7.1 10^3	.001164	.001162
3.	-.2	8.5 10^3	.001036	.001036
3.	-.1	1.4 10^4	.001999	.001994
3.	0.	1.9 10^4	.00285	.00284
2.8	-.2	1.8 10^4	.001942	.001936
2.8	-.1	2.7 10^4	.003426	.003411
2.	-.2	3.6 10^5	.02140	.02060
2.	.0	5.3 10^5	.03621	.03513
2.	.2	6.8 10^5	.04847	.04696
2.	.4	8.1 10^5	.05888	.05687

The helium atom is the simplest system where we can compare the predictions of the padded box model with the experimental results. The change in electronic kinetic energy can be calculated from the equation of state and experimental data are available for pressures up to 25 kbar[16]. It is well known that the hard box model over estimates by a few times the effect of pressure on the electronic kinetic energy. The padded box model allows one to fit the experimental data more closely (see Fig. 1), however there is no single value of U_0 which describes properly the behaviour of helium. Higher accuracy may be achieved when we consider U_0 as a function of the box radius (Fig. 1). It is interesting to notice that for the best fit of the experimental data the parameter γ (eq. (9)) for the Hartree-Fock orbital depends linearly on R (see Fig. 2). This observation may be important for the future development of the method if it is confirmed for the other systems.

The boundary perturbation method can be also applied for the hydrogen molecular ion H_2^+ enclosed in a spheroidal box (ξ_0 = const). The Schrodinger equation for H_2^+ separates in prolate spheroidal coordinates[10] and for the ground state it reads

$$[-\frac{1}{2}\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi} - R\xi - \frac{R^2\xi^2}{8}(2E - R^{-1})]\Phi = A(E)\Phi \qquad (18)$$

where R denotes the distance between hydrogen ions and ξ is an ellipsoidal coordinate defined as a sum of distances from both nuclei divided by R. The functional dependence of the separation constant A is given by an infinite series, the coefficients of which are well known[13]. It is easy to notice that equation (18) reduces to (10) when $h\equiv1$, $g(\xi)=\xi^2-1$, $H(E)=R^2/8\ (2E-R^{-1})$, $G(\xi)=\xi^2$, and $x_0=1$. As the first approach to the problem of the enclosed hydrogen molecular ion we have considered the case of the hard ellipsoidal box ($f(\xi_0)=0$). To test how accurate the boundary perturbation method is we repeated the calculations of Lee Koo and Cruz[10] for R=2 a.u. The results are presented in Table 3 and an

TABLE 3

Electronic energy (Rydberg units) of the ground state of H_2^+ molecular ion inside prolate spheroidal boxes of different sizes ξ_0 and eccentricities R = 2 a.u. E^{BPT} = boundary perturbation method, E = direct calculations[10].

ξ_0	E^{BPT}	E
4.4468	-2.19998	-2.2
2.9162	-2.05000	-2.05
2.4196	-1.75005	-1.75
2.2237	-1.50007	-1.50
2.0917	-1.24995	-1.25
1.9934	-1.00008	-1.00

excellent agreement between both methods can be observed.

Any realistic model of H_2^+ under pressure should take into account the change of the distance between nuclei. We have performed the calculations where for constant volume the shape of the box is changed to minimize the total energy. The total energy as a function of volume is shown in Fig. 3. It may be noticed that our result is below that obtained by Le Sar and Hershbach[7] who modelled H_2^+ using a variational form of the wavefunction in the box. In our model the distance between nuceli is shorter than that predicted by Le Sar and Hershbach (see Fig. 4). This is not surprising because Le Sar and Hershbach clearly overestimated the distance between nuclei suggesting that it is longer than 2 a.u. for low pressure. Our work on the properties of H_2^+ is still in progress, however it seems clear that the boundary perturbation method has proved its superiority over the variational approach for this system.

FINAL REMARKS

In concluding our discussion we emphasize that the boundary perturbation method (eq. (10)) is very general. It may be used to calculate the exact energy of a quantum state for any one-dimensional problem for both Dirichlet and Neumann boundary conditions and therefore it seems to be more appropriate than the variational approach where a very high accuracy of energy is required. The calculations for helium have shown that, in spite of the approximations involved, our boundary perturbation method works well for two-electron system for pressures up to 1 Mbar, which covers the range of pressures of interest for the study of chemical processes in detonations.

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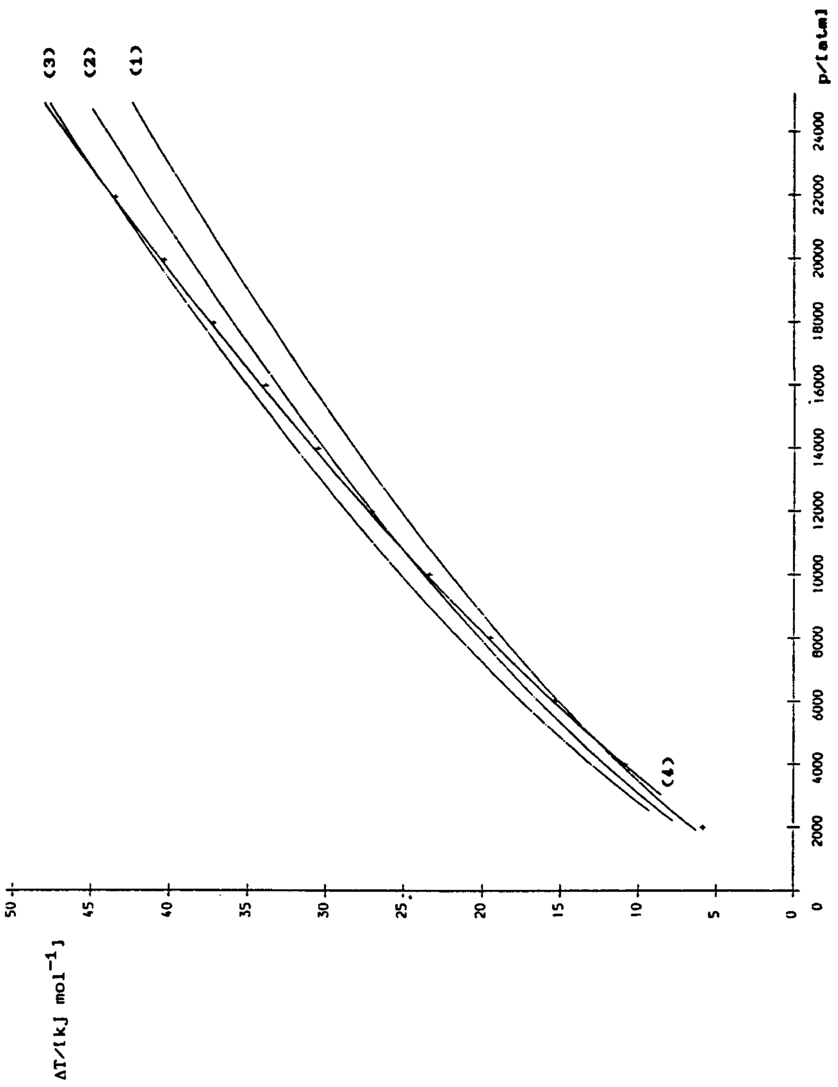

Fig 1.

Fig. 1

The comparison between the experimental value of the change in electronic kinetic energy of helium under pressure (crosses) and the results of the padded box model (line). Curve (1) corresponds to U_0 = -.18[a.u.], (2) to U_0 = -.16[a.u.], (3) to U_0 = 0.14[a.u.] and (4) to $U_0(R)$ = -.155 + 0.1*(3.5-R) [a.u.].

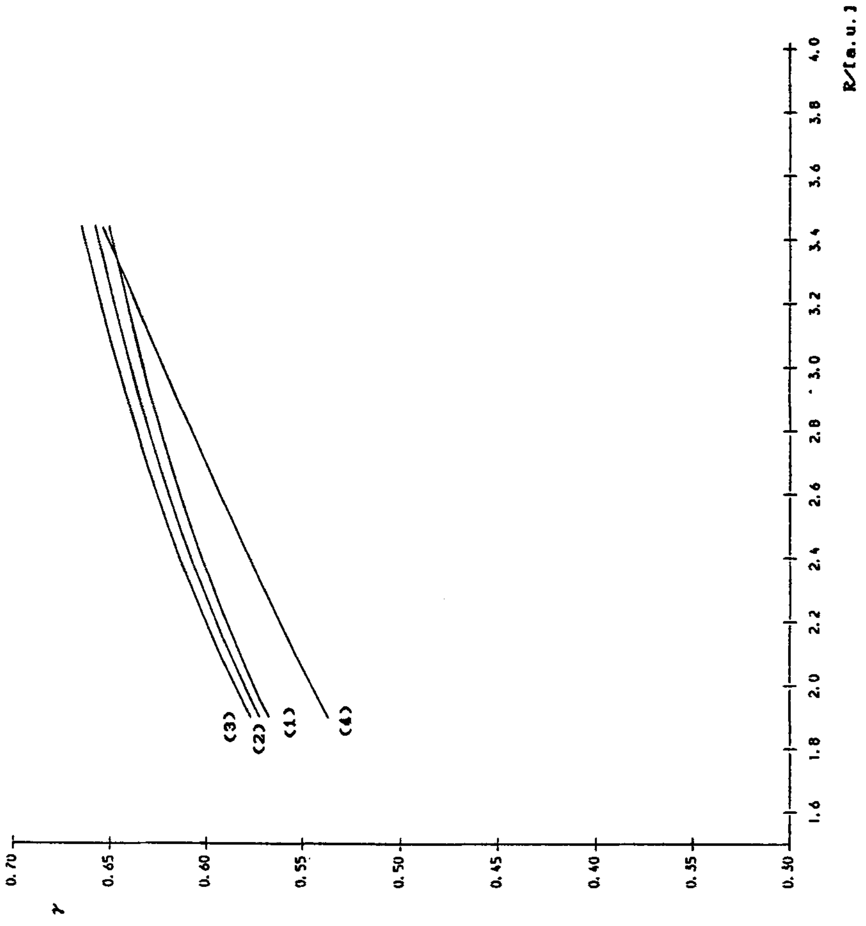

Fig 2.

Fig. 2

The parameter γ for the Hartree-Fock orbital of the ground state of the helium atom enclosed into a padded box (notation as for Fig. 1).

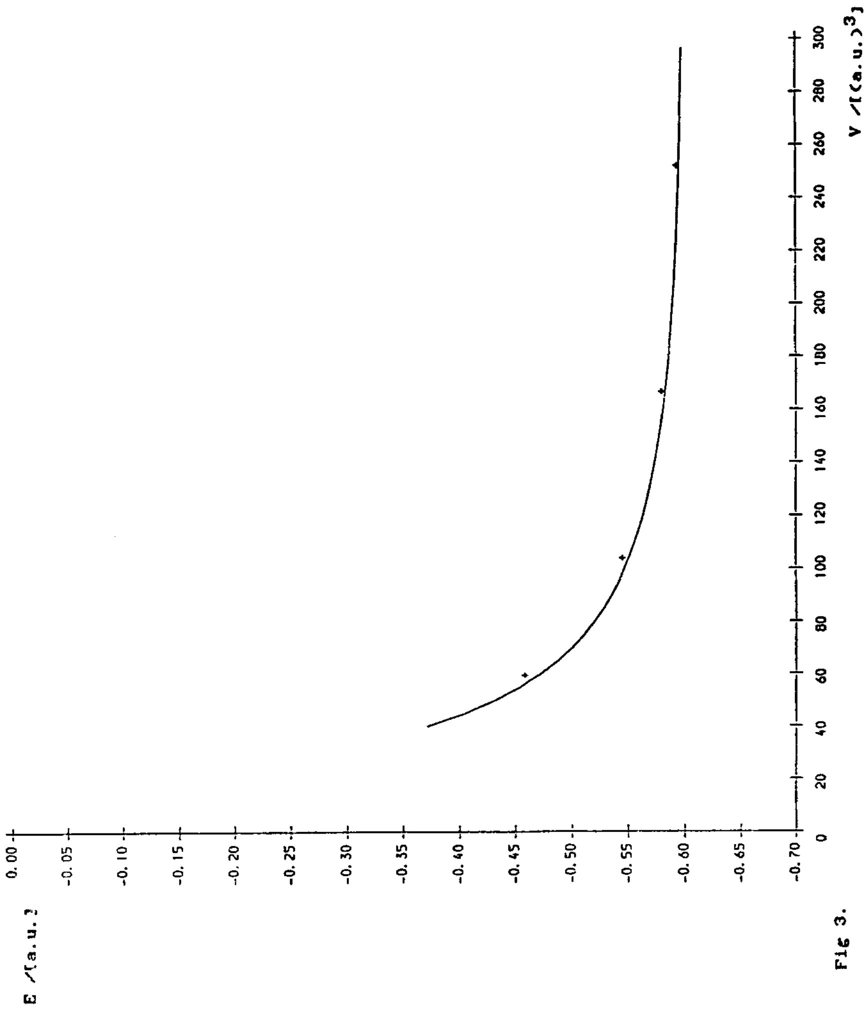

Fig. 3

The total energy of the hydrogen molecular ion H_2^+ enclosed in a box with unpenetrable walls (γ = 0) as a function of the box volume (line - boundary perturbation method, crosses - variational calculations[7]).

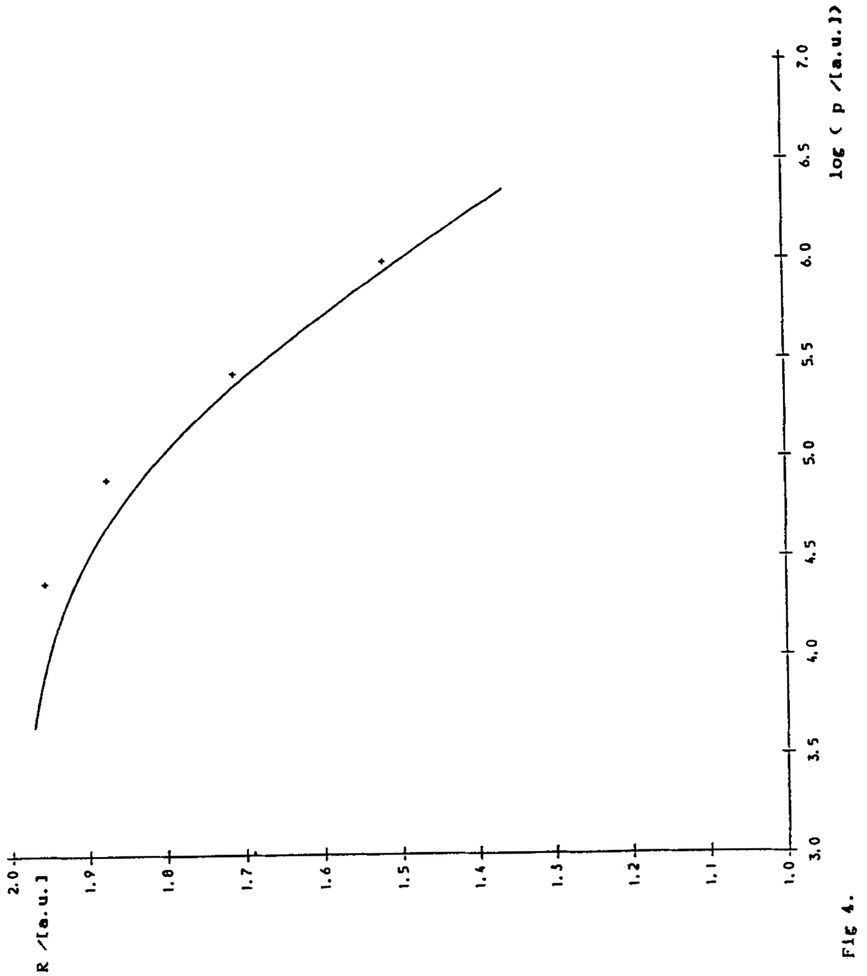

Fig. 4

The distance between the nuclei in the hydrogen molecular ion as a function of pressure (notation as in Fig. 3).