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LETTER TO THE EDITOR

APPLICATION OF THEORETICAL METHODS DEVELOPED IN MUON PHYSICS TO SOME PROBLEMS OF ATOMIC, MOLECULAR AND SOLID STATE PHYSICS

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The method which consists in the expansion of the wave function of the three-body Coulomb system over an adiabatic basis, and the reduction of the Schrödinger equation to the system of ordinary differential equations, can be successfully applied to some problems of atomic, molecular and solid state physics. We shall here present cross sections for the low energy electron (or positron) scattering on positronium (P_s) atoms, ground state energies obtained for simplest four-particle molecular systems, and the application of earlier three-particle mesomolecular calculations for the estimation of binding energies of similar excitonic systems.

The first observation of P^- was reported by Mills[1]. In this paper Mills suggested a number of interesting experiments. One of these experiments was photodetachment,

$$h\nu + P_s^- \rightarrow P_s + e^-.$$

In order to calculate cross section for this process a knowledge of the initial bound-state wave function and the continuum wave function for elastic scattering of slow electrons by P_s is required.

The elastic scattering of slow electrons by P_s is of interest in itself in the view of experiments on the scattering of P_s in gases, where the existence of a large electron (or positron) scattering cross section might have an important effect[2]. Such experiments would be of fundamental interest, since they provide a test of charge conjugation in leptonic systems $e^+ e^- e^-$. If σ_+ is the cross section for positron impact on P_s and σ_- is cross section for electron impact then, if charge conjugation holds, $\eta = \sigma_+/\sigma_- \equiv 1$. An experiment will set a bound.

Recently, we finished our calculations for elastic and spin-flip scattering processes of electron on positronium atom in para and ortho state in the $\varepsilon < 0.05$ eV energy region; elastic and symmetric charge exchange cross sections for the same system were calculated without spin interaction for the scattering energies $\varepsilon < 4$ eV[3]. Low energy scattering with spin-flip processes has been treated for the first time.

In the framework of the adiabatic method, an excellent result was obtained for the ground state binding energy of $e^+ e^+ e^-$ system[4], indicating that this method can be confidentely used even in the case when the adiabatic »small« parameter M (the reduced mass of particles of equal charges in units of atomic reduced mass) is equal to one.

This fact encourages us to try to investigate the scattering processes in the electron positron three particle systems:

$$\begin{tikzcd}
e^+ e^- (F = 1) + e^- \arrow[r, "\sigma^s_{22}"] \arrow[dr, "\sigma^s_{21}"'] & e^+ e^- (F = 1) + e^- \\
e^+ e^- (F = 0) + e^- \arrow[r, "\sigma^s_{11}"'] \arrow[ur, "\sigma^s_{12}"'] & e^+ e^- (F = 0) + e^-,
\end{tikzcd} \tag{1}$$

where σ^s_{ij} are cross sections for respective processes.

The difference between $F = 1$, and $F = 0$ levels of $e^+ e^-$ atom ($\vec{F} = \vec{I} + \vec{J}$, where $\vec{I}$ is electron and $\vec{J}$ is positron spin) is $\Delta\varepsilon_{hfs} = 0.000835$ eV.

In the reaction (1) σ^s_{11} and σ^s_{22} are elastic scattering cross sections for $e^+ e^-$ atoms scattering in para and ortho states ($F = 0$ and $F = 1$ respectively) on electron; σ^s_{12} and σ^s_{21} cross sections represent transition between those states; $\vec{S}$ is total spin of $e^+ e^- + e^-$ system. Because of the obvious symmetry reasons, the same cross sections are valid for positronium scattering on the positronium atoms.

Taking into account only exchange interaction which conserves total spin $\vec{S} = \vec{F} + \vec{I}_2 = \vec{I}_1 + \vec{I}_2 + \vec{J}$, and neglecting spin interaction of electrons, levels can be also classified according to the value of total spin of $e^+ e^-$ system: $F = = \frac{1}{2} \pm \frac{1}{2}$ [5,6].

In the low energy collision region $\varepsilon < 0.05$ eV only ground state of $e^+ e^-$ atom should be considered, i. e. two lower reaction channels can be open: channel 1 with spin $F = 0$ and channel 2 with $F = 1$. As to our knowledge, this is the first attempt to treat theoretically proces (1) in this energy region.

The low energy collisions in a three body problem can be tackled by means of the multichannel scattering theory. In the case of comparable masses a great number of closed channels have to be taken into account[7]. For instance, the work devoted to the scattering of $d\mu$-atom on deuterium nuclei[6], about 100 closed channels (of discrete and continuous spectrum of two-centre Coulomb problem) were enough to obtain cross sections σ'_{ij} with the accuracy $\lesssim 5\%$ for energy region $\varepsilon \leqslant 1$ eV.

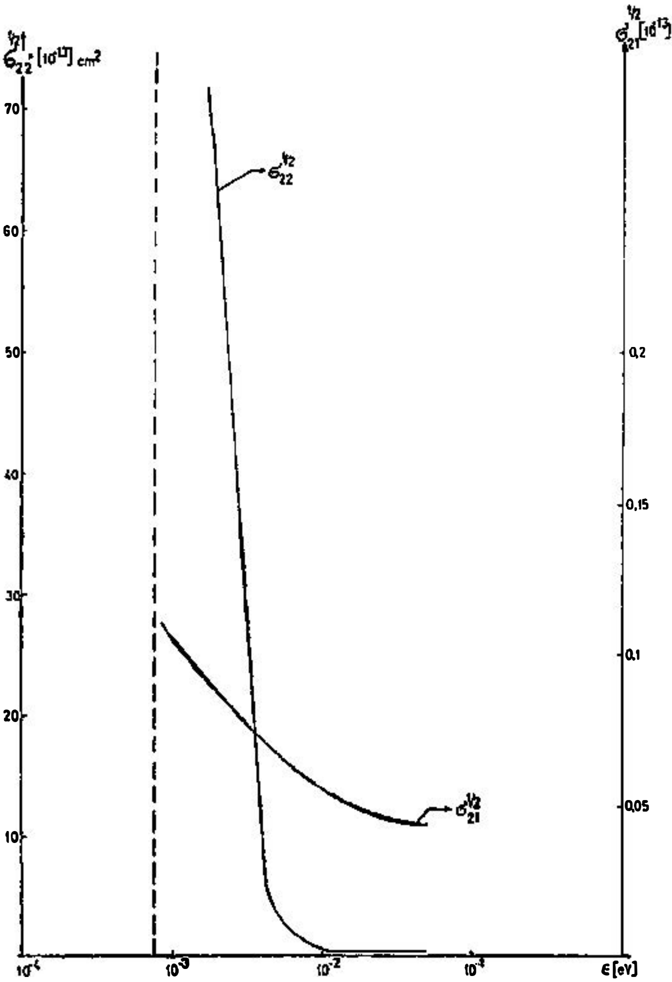

Fig. 1. Elastic scattering s-wave cross sections $\sigma_{22}^{1/2}(\varepsilon)$ of ortho e^+e^- atoms ($F = 1$) and ortho-para $\sigma_{21}^{1/2}(\varepsilon)$ transition in the low energy region ($\sigma_{22}^{1/2} = 89 \cdot 10^{-13}$ cm^2 for $\varepsilon = 0.85 \cdot 10^{-3}$ eV).

The transition from $e^+ e^-$ state $F_1 = 1$ to the state $F_2 = 0$ is possible only for the case $S = 1/2$. The state with total three particle spin $S = 3/2$ does not include level with positronium spin $F_2 = 0$, if we suppose the conservation of total spin S. Fig. 1 give the results for the $\sigma_{22}^{1/2}$ and $\sigma_{21}^{1/2}$ cross sections versus collision energy $\varepsilon = \frac{k^2}{2}$ of the $e^+ e^- + e^-$ system. The *s*-wave cross sections are only shown in that picture. All results were obtained for $N = 6$ coupled adiabatic equations with proper boundary conditions. Our results presented on Fig. 1 give $\approx$ 60—70% of the σ'_{ij} for the scattering of electrons on P_s atoms (more detailed discussion can be found in Ref. 3).

All principal problems for the inclusion of higher discrete and continuous states were solved$^{6,7)}$ and more precise scattering cross section could be obtained with relatively straightforward computing work.

Besides above spin induced processes, we have also calculated processes of the elastic scattering $e^+ e^- + e^- \rightarrow e^+ e^- + e^-$ and symmetric charge exchange $e^+ e^- + e^- \rightarrow e^- + e^+ e^-$, by taking into account only the Coulomb interaction between charged particles. The results for these processes are given in Fig. 2. In this figure the contribution of *p*-partial wave is presented also.

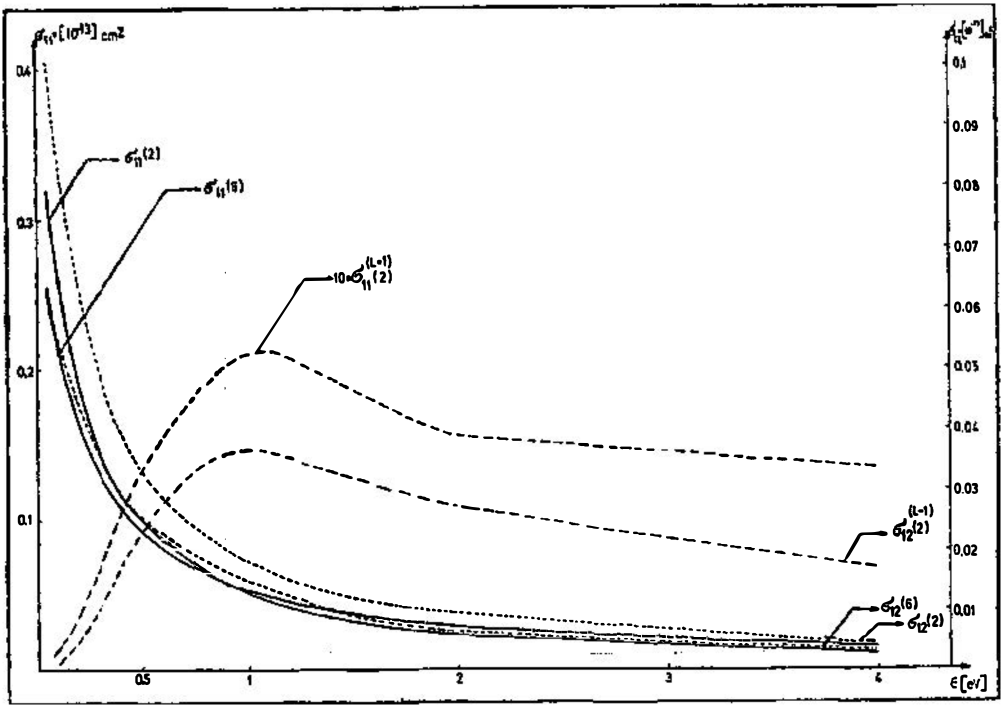

Fig. 2. Elastic scattering and symmetric charge exchange *s*-wave cross sections $\sigma_{11}(N)$ and $\sigma_{12}(N)$ ($N = 2$ or 6), respectively. We also presented *p*-wave cross sections $\sigma_{11}^{(L=1)}(2)$ and $\sigma_{12}^{(L=1)}(2)$.

In conclusion of this part it could be said that reasonable numerical results have been obtained, indicating that adiabatic method can be applied for the calculation of low energy scattering processes of particles with equal masses interacting via Coulomb and contact spin interactions.

Another interesting problem where adiabatic method for scattering processes can be applied is the antihydrogen formation in collisions of antiprotons with positronium[8]. We are working on this problem now. Antihydrogen $\overline{\mathrm{H}}$ is one of the most fundamental systems in physics and studies of its properties and interactions will, for example, allow a critical test of CPT invariance. Unlike to exotic atoms, such as positronium, muonium and protonium, $\overline{\mathrm{H}}$ is stable and may therefore provide a more ideal system for testing fundamental questions in physics.

Variational results for the formation cross section of antihydrogen in upper mentioned collisions can be obtained from the formation cross section of hydrogen in collisions of P_s with protons, while this cross section is, by time reversal invariance, simply related to the cross section for P_s formation in positron hydrogen collisions. These results depend very essentially of the trial functions which were used[8,9].

Several years ago we tried to apply the adiabatic basis to simplest molecules. The two-centre functions of this basis have the advantage when applied to diatomic molecules because the electron interaction with the Coulomb field of two nuclei is more adequately treated and, as they are orthogonal, the overlapping integrals are equal to zero.

When the adiabatic basis is applied to two-electron diatomic molecules, one gets an infinite system of differential equations for the total molecular energy E of these systems (details and the corrected formulation of the method can be found in Ref. 10):

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}R^2} + 2M(E - E_i(R))\right] \chi_i(R) = \sum_j \langle i|V|j\rangle \chi_j(R). \qquad (2)$$

Here R is the distance between positive particles, M is the reduced mass of the same particles in the units of the atomic reduced mass $m_a^{-1} = (M_a^{-1} + m_e^{-1})$, $M = (M_a^{-1} + M_b^{-1})^{-1}/m_a$ $(M_a \geq M_b)$, $E_i(R)$ are effective terms, $\langle i|V|j\rangle$ denotes effective potentials, and $\chi_i(R)$ are the components of the radial part of the molecular wave function. Note that index i corresponds to the pair of indices $i \equiv (m, n)$. This is influenced by the obvious necessity to expand the total molecular wave function over symmetrized products of two-centre functions $\Phi_m(\vec{r}_1; R) \cdot \Phi_n(\vec{r}_2; R)$ ($\vec{r}_1$ and $\vec{r}_2$ are electronic coordinates relative to the centre of the vector $\vec{R}$).

The system (2) contains unknown matrix elements of the electron repulsion operator r_{12}^{-1} over two-centre functions. The other terms of effective potentials can be expressed through matrix elements characteristic of the molecular hydrogen ion in the adiabatic basis.

The main obstacle for the application of the adiabatic basis in the theory of diatomic molecules is connected with the calculation of the Coulomb repulsion r_{12}^{-1} matrix elements. This problem has been solved in principle[11]. We know which terms of the Neumann expansion of the operator r_{12}^{-1} are relevant, and we can write down the general formulae for the respective matrix elements over two-centre functions. The numerical calculations of these matrix elements are time consuming and requires a lot of intermediate information to be calculated and stored. The most interesting result were obtained when our method was applied for the calculation of the ground state energies of excitonic molecules, where al Coulombic centres have comparable effective masses. The nonadiabatic terms cannot be taken into account by the perturbation theory, as has been usually done when calculating properties of ordinary molecules. In our approach the nonadiabatic corrections are separated explicitly thus allowing more natural investigations of their influence. These terms were already calculated in connection with mesomolecular physics, and stored in Ref. 12. At present we have 58 Coulomb repulsion matrix elements relating all σ-states ($1g$, $1u$, $2g$, $2u$, $3g$, $3u$) from the first and second shell[11]. If these terms are taken into account the system of differential equations (2) reduces to twenty one coupled second order differential equations. This system has been solved on the JINR CDC-8500 computer by the program SYSTEM[13]. We have now this program adapted for the VAX 11/751 computer also.

Our results for the ground state energies of biexciton as a function of electron to hole mass ratio are given in Fig. 3.

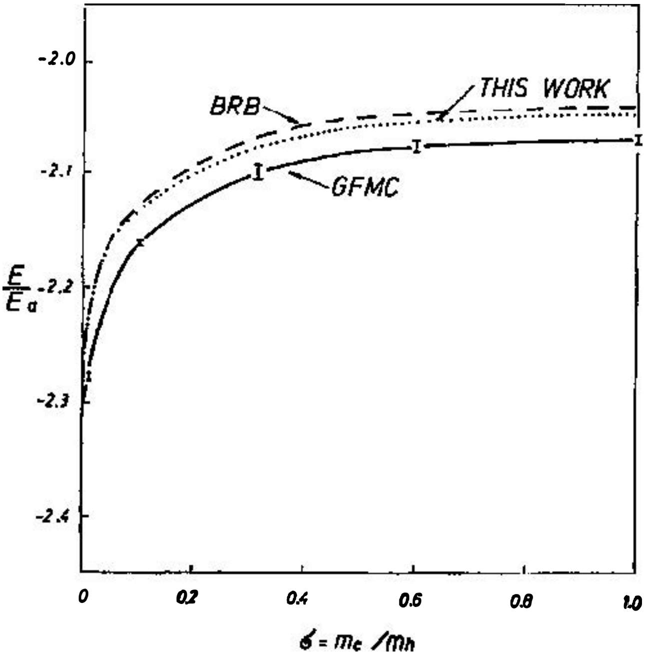

Fig. 3. Ground state energies of biexcitons as a function of electron-hole mass ratio, σ. The dashed curve represents variational results of Brinkman, Rice and Bell (BRB)[14], the solid curve shows Green's function Monte Carlo (GFMC) results[15], while dotted curve represents our results. Here energies are represented in excitonic Rydbergs, E_a.

In conclusion of this part it can be said that the adiabatic method produces a noticable increase in binding energies of excitonic molecular systems, as compared to previous variational calculations. This is accomplished in the simplest realization of the method with π-terms rejected. The increase in binding energies is about 15% practically in the whole $\sigma = m_e/m_h$ region. In that way we have shown that a more careful choice of basis functions and a consistent inclusion of nonadiabatic corrections are the reasons for such an increase in binding energies. Even greater successes should be expected after the application of the compatible adiabatic basis (CAB)$^{16)}$ to the simplest molecules. The usage of CAB excludes the continuous spectrum of the two-centre problem, which always appears in standard adiabatic approach.

The last issue which we want to discuss concerns some scaling relations for the ground state energies of three-particle systems with Coulomb interaction. We recently suggested the general approximate expression for the nonrelativistic ground state energies of Coulomb systems with charges $Z_a = Z_b = \pm 1$ and $Z_c = \mp 1$ and arbitrary masses M_a, M_b and M_c.

The development of computers in recent years has made it possible to transform variety of methods of quantum mechanics and quantum chemistry into respective numerical algorithms. Numerical calculations are always approximate. Anyone who has developed some complicate numerical program for treating many particle systems, knows how important, for checking the accuracy, are exact relations, which follow from quantum mechanics. A very interesting review of the possibilities to obtain such exact relations in quantum theory of atoms and molecules can be found in recent monograph by Rebane and Penkina$^{17)}$. This monograph is devoted to the investigation of regularities which result from the scaling transformation of coordinates, and variational principle of quantum mechanics. The important ingredient of the relations obtained in Ref. 17 is that they do not contain wave functions. These relations connect directly measurable quantities of similar quantum systems.

The general formula for the ground state energy limits can be relatively successful only in the case $M_a = M_b \neq M_c$ (cf. Ref. 17 page 165). It has to be noted that the limits for the ground state energies become crude in the case of the considerable changes of ratios of particle masses.

With this fact in mind, the direct interpolation procedures become interesting. One of the attempts, which uses the scaling transformation of coordinates and the expansion of energy in the powers of the Born-Oppenheimer parameter, made it possible to derive the formula for the ground state energy of three-particle Coulomb symmetric systems $(M_a = M_b = m)^{18)}$:

$$E(m, m, M_c) = m\, \beta\, \varepsilon(\beta) \tag{3}$$

where $\beta = M_c/(2m + M_c)$ and $\varepsilon(\beta)$ is the function of β defined in the interval $0 < \beta < 1$. The knowledge of this function makes it possible to find ground state energies of all Coulomb systems with masses $M_a = M_b = m$ and M_c and charges Z_a, Z_b and Z_c. In Ref. 18 the following approximate expansion of the function ε in the powers of the Born-Oppenheimer parameter $\beta^{1/4}$ was suggested:

$$\varepsilon(\beta) = \sum_{j=1}^{5} c_j\, \beta^{j/2}. \tag{4}$$

Unknown coefficients were determined on the basis of the very precisely known ground-state energies of six standard systems. The standard systems were chosen to cover the interval of variations of β as wide as possible. The formula (4) is obtained without any assumptions about the adiabatic separation of variables, so it is valid for true nonrelativistic energies of three-particle systems. But the choice of standard systems in Ref. 18 limited the application of formula (4) only to the cases where $Z_a = Z_b = \pm 1$, $Z_c = \mp 1$ and $M_a = M_b = m$.

Many interesting muonic, excitonic etc. systems, with $M_a \neq M_b$ are beyound the scope of formulae (3) and (4).

We have attempted to find some analytical scaling relations which connect total ground state energies of these systems. After many unsuccessful attempts, we realized that, with remarkable exactness, the following simple empirical formula can be used ($Z_a = Z_b = \pm 1$, $Z_c = \mp 1$):

$$E(M_a, M_b, M_c) = \frac{1}{2}\left[E(M_a, M_b, M_c) + E(M_b, M_b, M_c)\right]. \tag{5}$$

The results obtained using this formula for the ground state energies of some molecular and mesomolecular systems are given in the Table 1.

TABLE 1.

molecule	$E_{1/2}$ (eV)	E_{var} (eV)	$(E_{1/2} - E_{var})/E_{var}$
$pd\mu$	−2884.70	−2884.4219	$1.55 \cdot 10^{-5}$
$pt\mu$	−2927.675	−2924.1816	$1.19 \cdot 10^{-3}$
$dt\mu$	−3031.055	−3029.2516	$5.94 \cdot 10^{-4}$
pde	−16.271017	−16.269258	$1.08 \cdot 10^{-4}$

Total molecular ground state energy E obtained on the basis of formulae (3—5). E_{var} represent results of variational calculations of the same quantity (these results are almost the same as adiabatic results presented in Ref. 4).

The accuracy of the results given in Table 1 is extremely good, bearing in mind the differencies between the results obtained with much more complicated and laborous methods (cf. Tables 1—5 from Ref. 4).

In conclusion, we want to emphasize that it is now possible to obtain nonrelativistic ground state energies of all three-particle Coulomb systems very easily and precisely (formulae (3), (4) and (5)). For the time being, the only limitation is $Z_a = Z_b = \pm 1$, $Z_c = \mp 1$. At first sight, this looks like a very sharp limitation. But, a large number of mesonic and excitonic systems can be treated by our method.

As an illustration, we shall present the calculation of the ground state energy of exciton ionized donor complex in CdSI system. This system was investigated experimentally, as well as theoretically[19].

The fundamental constants of CsSI are $m_e^* = 0.18$, $\sigma = m_e^*/m_h^* = 0.182$ (masses are given in units of the electron mass m_e). The values of dielectric constant for an atom consisting of an electron and an ionized donor, and for excitonic atom are $K_D = 9.031$ and $K_x = 8.7578$, respectively.

Applying formulae (3) and (5) (details are given in Ref. 20) one easily get:

$$E(\infty, m_h^*, m_e^*) = -32.7445 \, \text{meV}.$$

This value is to be compared with experimental total energy of this system, which is equal to $E^{\text{exp}} = -33.22$ meV, and the theoretical value obtained by means of much more complicated anysotropic variational calculations $E^{\text{calc}} = -30.9701$ meV[19]. Our result is in much better agreement with experiment ($|\Delta E|/E^{\text{exp}} = 2.6\%$) than the variational value ($|\Delta E^{\text{calc}}|/E^{\text{exp}} = 7.9\%$).

This example, together with Table 1, shows the obvious advantage of the method we suggested. Although our method is very simple and empirical one, for the time being, its predicting possibility is surprising and it gives excellent results in all examples we tested. The difference between the experimental total energy of the three-particle excitonic systems and the value obtained from the formula (5) can be used for the estimation of the anysotropy of effective masses of electrons and holes in semiconductors.

We hope that similar scaling relations could be found for other types of interactions.

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PRIMENA TEORIJSKIH METODA RAZVIJENIH U MEZONSKOJ FIZICI ZA ISPITIVANJE NEKIH PROBLEMA ATOMSKE, MOLEKULARNE I FIZIKE ČVRSTOG STANJA

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Metod, u okviru koga se talasna funkcija tročestičnog kulonovskog sistema razvija po adiabatskom bazisu i Schroedingerova jednačina redukuje na sistem običnih diferencijalnih jednačina, može se uspešno primeniti za ispitivanje nekih problema atomske, molekularne i fizike čvrstog stanja. U ovom radu dajemo rezultate za preseke niskoenergetskog rasejanja elektrona (ili pozitrona) na atomima pozitronijuma (P_s), energije osnovnog stanja najprostijih četvoročestičnih molekularnih sistema i primenu ranijih tročestičnih mezomolekularnih proračuna za određivanje energija veze sličnih eksitonskih sistema.