

Walter Thirring

A Course in Mathematical Physics

3

Quantum Mechanics of Atoms and Molecules

Translated by Evans M. Harrell

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Preface

In this third volume of *A Course in Mathematical Physics* I have attempted not simply to introduce axioms and derive quantum mechanics from them, but also to progress to relevant applications. Reading the axiomatic literature often gives one the impression that it largely consists of making refined axioms, thereby freeing physics from any trace of down-to-earth residue and cutting it off from simpler ways of thinking. The goal pursued here, however, is to come up with concrete results that can be compared with experimental facts. Everything else should be regarded only as a side issue, and has been chosen for pragmatic reasons. It is precisely with this in mind that I feel it appropriate to draw upon the most modern mathematical methods. Only by their means can the logical fabric of quantum theory be woven with a smooth structure; in their absence, rough spots would inevitably appear, especially in the theory of unbounded operators, where the details are too intricate to be comprehended easily. Great care has been taken to build up this mathematical weaponry as completely as possible, as it is also the basic arsenal of the next volume. This means that many proofs have been tucked away in the exercises. My greatest concern was to replace the ordinary calculations of uncertain accuracy with better ones having error bounds, in order to raise the crude manners of theoretical physics to the more cultivated level of experimental physics.

The previous volumes are cited in the text as I and II; most of the mathematical terminology was introduced in volume I. It has been possible to make only sporadic reference to the huge literature on the subject of this volume—the reader with more interest in its history is advised to consult the compendious work of Reed and Simon [3].

Of the many colleagues to whom I owe thanks for their help with the German edition, let me mention F. Gesztesy, H. Grosse, P. Hertel, M. and T.

Hoffmann-Ostenhof, H. Narnhofer, L. Pittner, A. Wehr, E. Weimar, and, last but not least, F. Wagner, who has transformed illegible scrawls into a calligraphic masterpiece. The English translation has greatly benefited from the careful reading and many suggestions of H. Grosse, H. Narnhofer, and particularly B. Simon.

Vienna
Spring, 1981

Walter Thirring

Symbols Defined in the Text

p, q	momentum and position coordinates	
ψ	Schrödinger wave function	
\hbar	Planck's constant	
L	orbital angular momentum	
l	angular momentum quantum number	
Z	nuclear charge	
r_b	Bohr radius	(1.2.3)
R_y	Rydberg	(1.2.4)
E	vector space	(2.1.1)
C	set of complex numbers	(2.1.1)
$\ \cdot \ $	norm	(2.1.4)
$\ \cdot \ _p$	p -norm	(2.1.5; 6)
$L^p(K, \mu)$	space of p -integrable functions on K	(2.1.5; 6)
l^p	sequence space	(2.1.6; 2)
$\langle \cdot \cdot \rangle$	scalar product	(2.1.7)
e_γ	basis vector	(2.1.12; 3)
E'	dual space to E	(2.1.16)
$\mathcal{L}(E, F)$	space of continuous, linear mappings from E to F	(2.1.24)
$\mathcal{B}(E)$	space of bounded operators on E	(2.1.24)
a^*	adjoint operator for a	(2.1.26; 3)
$w\text{-lim}, \rightarrow$	weak limit	(2.1.27)
$s\text{-lim}, \rightarrow$	strong limit	(2.1.27)
\lim, \Rightarrow	norm limit	(2.1.27)
l^0	sequence space	(2.2.2)
$Sp(a)$	spectrum of a	(2.2.13)
$a \geq b$	partial ordering of operators	(2.2.16)
$X(\mathcal{A})$	set of characters	(2.2.25)
$(\Delta_w(a))^2$ = $(\Delta a)^2$ = Δa^2	mean-square deviation	(2.2.33; 3)

\mathcal{P}	propositional calculus	(2.2.35)
$p_1 \wedge p_2$	intersection of propositions	(2.2.35(i))
$p_1 \vee p_2$	union of propositions	(2.2.35(ii))
$\sigma_x, \sigma_y, \sigma_z$	spin matrices	(2.2.37)
π	representation	(2.3.1)
\mathcal{M}'	commutant of \mathcal{M}	(2.3.4)
\mathcal{Z}	center	(2.3.4)
$\theta(x)$	step function	(2.3.14)
$\sigma_p(a)$	point spectrum	(2.3.16)
σ_{ac}	absolutely continuous spectrum	(2.3.16)
$\sigma_s(a)$	singular spectrum	(2.3.16)
σ_{ess}	essential spectrum	(2.3.18; 4)
$\text{Tr } m$	trace of m	(2.3.19)
\mathcal{C}_1	trace-class operators	(2.3.21)
\mathcal{C}_2	Hilbert-Schmidt operators	(2.3.21)
\mathcal{C}	compact operators	(2.3.21)
T	time-ordering	(2.4.10; 3)
$D(a)$	domain of definition of a	(2.4.12)
$\text{Ran}(a)$	range of a	(2.4.12)
$\Gamma(a)$	graph of a	(2.4.15)
$a \supset b$	a extends b	(2.5.1)
$Q(q)$	quadratic-form domain	(2.5.17)
\mathscr{W}	Weyl algebra	(3.1.1)
$(z z')$	scalar product	(3.1.2; 1)
$ l, m\rangle$	angular momentum eigenvectors	(3.2.13)
L_{\pm}	circular components of L	(3.2.13)
$\text{ad}_H^n(a)$	(derivation) ⁿ	(3.3.1)
P_{ac}	projection onto the absolutely continuous eigenspace	(3.4.4)
\mathcal{A}	algebra of asymptotic constants	(3.4.6)
a_{\pm}	limit of an asymptotic constant	(3.4.6)
τ_{\pm}	homomorphism $\mathcal{A} \rightarrow \mathcal{A}_{\pm}$	(3.4.6)
Ω_{\pm}	Møller operators	(3.4.7; 4)
P_a	projection for the channel with H_a	(3.4.17)
$Q_{a\pm}$	channel decomposition of P_{ac}	(3.4.17)
$S_{\alpha\beta}$	S matrix in the interaction representation	(3.4.23)
$R(\alpha, z)$	resolvent	
$P_k(\alpha)$	projection operator for the perturbed Hamiltonian $H(\alpha)$	(3.5.1)
$t(k)$	t matrix	
$f(k; n', n)$	angular dependence of the outgoing spherical wave	(3.6.10; 3)
D	delay operator	(3.6.17)
$\sigma(k, k_0)$	differential scattering cross-section	(3.6.19)
σ_t	total scattering cross-section	(3.6.19)
a	scattering length	(3.6.23; 5)
F	Runge-Lenz vector	(4.1.7)
A_k, B_k	generators of $O(4)$	(4.1.8)

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1.1 The Structure of Quantum Theory

The structure of quantum mechanics differs startlingly from that of the classical theory. In volume I we learned that in classical mechanics the observables form an algebra of functions on phase space (p and q), and states are probability measures on phase space. The time-evolution is determined by a Hamiltonian vector field. It would be reasonable to expect that atomic physics would distort the vector field somewhat, or even destroy its Hamiltonian structure; but in fact the break it makes with classical concepts is much more drastic. The algebra of observables is no longer commutative. Instead, position and momentum satisfy the famous **commutation relations**,

$$qp - pq = i\hbar. \quad (1.1.1)$$

Since matrix algebras are not generally commutative, one of the early names for quantum theory was matrix mechanics. It became apparent in short order, however, that the commutator (1.1.1) of finite-dimensional matrices can never be proportional to the identity (take the trace of both sides), so attempts were then made to treat p and q as infinite-dimensional matrices. This proved to be a false scent, since infinite-dimensional matrices do not provide an ideal mathematical framework. The right way to proceed was pointed out by J. von Neumann, and the theory of C^* and W^* algebras today puts tools for quantum theory at our disposal, which are polished and comparatively easy to understand. There do remain a few technical complications connected with unbounded operators, for which reason the **Weyl relation**

$$e^{iaq}e^{i\beta p}e^{-iaq} = e^{i\beta(p-a)} \quad (1.1.2)$$

(setting $\hbar = 1$) is a better characterization of the noncommutativity.

Admittedly, Schrödinger historically first steered quantum mechanics in a different direction. The equation that bears his name treats p and q as differentiation and multiplication operators acting on the **Schrödinger wave-function** ψ , which has the interpretation of a **probability amplitude**: It is complex-valued, and $|\psi|^2$ is the probability distribution in the state specified by ψ . Superposition of the solutions of the equation causes **probability interference effects**, a phenomenon that can not be understood classically at all. Later, ψ was characterized axiomatically as a vector in Hilbert space, but the peculiar fact remained that one worked with a complex Hilbert space and came up with real probabilities.

At long last the origin of the Hilbert space was uncovered. A state would normally be required to be represented as a **positive linear functional**, where positivity means that the expectation value $\langle a^2 \rangle$ of the square of any real observable a must always be nonnegative. It turns out that to each state there corresponds a representation of the observables as linear operators on some Hilbert space. (It is at first unsettling to learn that each state brings with it its own representation of the algebra characterized by (1.1.2), but it also turns out that they are all equivalent.) The schema of quantum theory thus adds no new postulates to the classical ones, but rather omits the postulate that the algebra is commutative. As a consequence, quantum mechanically there are no states for which the expectation values of all products are equal to the products of the expectation values. Such a state would provide an algebraic isomorphism to the ordinary numbers, which is possible only for very special noncommutative algebras. The occurrence of nonzero fluctuations $\langle \Delta a \rangle^2 \equiv \langle a^2 \rangle - \langle a \rangle^2$ is in general unavoidable, and gives rise to the indeterministic features of the theory. The extremely good experimental confirmation of quantum mechanics shows that the numerous paradoxes it involves are owing more to the inadequacy of the understanding of minds raised in a classical environment than to the theory.

Quantum theory shows us where classical logic goes awry; the logical maxim *tertium non datur* is not valid. Consider the famous double-slit experiment. Classical logic would reason that if the only and mutually exclusive possibilities are “the particle passes through slit 1” and “the particle passes through slit 2,” then it follows that “the particle passes through slit 1 and then arrives at the detector” and “the particle passes through slit 2 and then arrives at the detector” are likewise the only and mutually exclusive possibilities. **Quantum logic** contests this conclusion by pointing to the irreparable change caused in the state by preparing the system to test the new propositions. The rules of quantum logic can be formulated just as consistently as those of classical logic. Nonetheless, the world of quantum physics strikes us as highly counterintuitive, more so even than the theory of relativity. It requires radically new ways of thinking.

The mathematical difficulties caused by the noncommutativity have all been overcome. Indeed, the fluctuations it causes often simplify problems. For example, the fluctuations of the kinetic energy, the **zero-point energy**,

have the effect of weakening the singularity of the Coulomb potential and eliminating the problem of the collision trajectories, which are so troublesome in classical mechanics. Quantum theory guarantees that the time evolution can be continued uniquely from $t = -\infty$ to $t = +\infty$ for (non-relativistic) systems with $1/r$ potentials. In a certain sense this potential energy is only a small perturbation of the kinetic energy, and free particles can be used as a basis of comparison. Calculations are sometimes much easier to do in quantum theory than in classical physics; it is possible, for instance, to evaluate the energy levels of helium with fantastic precision, whereas only relatively crude estimates can be made for the corresponding classical problem.

1.2 The Orders of Magnitude of Atomic Systems

One can come to a rough understanding of the characteristics of quantum-mechanical systems by grafting discreteness and fluctuations of various observables onto classical mechanics. Their magnitudes depend on **Planck's constant** \hbar , which is best thought of as a quantum of angular momentum, since quantum-mechanically the orbital angular momentum L takes on only the values $l\hbar$, $l = 0, 1, 2, \dots$. Suppose an electron moves in the Coulomb field of a nucleus of charge Z ; then the energy is

$$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{Ze^2}{r}. \quad (1.2.1)$$

For circular orbits ($p_r = 0$), quantization of the angular momentum means that

$$E(r) = \frac{l^2 \hbar^2}{2mr^2} - \frac{Ze^2}{r}. \quad (1.2.2)$$

At the radius

$$r = \frac{l^2 \hbar^2}{mZe^2} \equiv \frac{l^2 r_b}{Z}, \quad (1.2.3)$$

where r_b is known as the **Bohr radius**, the energy is minimized, with the value

$$E = -\frac{(Ze^2)^2 m}{2 l^2 \hbar^2} = \frac{-Z^2 e^2}{l^2} \frac{1}{2r_b} \equiv -\frac{Z^2}{l^2} (\text{Rydberg} \equiv \text{Ry}) \quad (1.2.4)$$

(**Balmer's formula**). If $l = 0$, then we would find $r = 0$ and $E = -\infty$, except that the stability of the system is saved by the inequality for the fluctuations $\Delta p \Delta q \geq \hbar/2$, the **indeterminacy relation**, which follows from (1.1.1). This makes $\langle p_r^2 \rangle \geq (\Delta p_r)^2 \approx \hbar^2/r^2$, the **zero-point energy**, and hence this part of

the kinetic energy contributes as much as a centrifugal term with $l = 1$. This argument actually gives the correct ground-state energy. The reasoning is of course not a mathematically rigorous deduction from the indeterminacy relation, as the average of $1/r$ could conceivably be large without Δr being small. We shall later derive generalizations of the inequality $\Delta p \Delta q \geq \hbar/2$, which will justify the argument.

The virial theorem states that the velocity v of an electron is given classically by

$$\frac{mv^2}{2} = -E = \frac{Z^2 e^4 m}{2l^2 \hbar^2} \Rightarrow v = \frac{Z e^2}{l \hbar}.$$

The universal speed e^2/\hbar is about $1/137$ times the speed of light. As Z increases, the nonrelativistic theory rapidly loses its accuracy. Relativistic corrections, entering through the increase of the mass and magnetic interactions, are $\sim v^2/c^2 \approx 10^{-5} Z^2$. For small Z they show up as fine structure of the spectral lines, but their effect becomes pronounced for heavy nuclei, and when Z is sufficiently greater than 137 the system is not even stable anymore. The relativistic kinetic energy is $\sqrt{m^2 c^4 + p^2 c^2} - mc^2$, which for large momenta grows only as $cp \approx \hbar/r$. Equation (1.2.2) is accordingly changed to

$$E(r) \approx \frac{\hbar c}{r} - \frac{Ze^2}{r} = \frac{\hbar c}{r} \left(1 - \frac{Z}{137}\right), \quad (1.2.5)$$

which is no longer bounded below when $Z > 137$. The question of what happens for such large Z can only be answered in the relativistic quantum theory, and lies beyond the scope of this book.

If a second electron is introduced to form a helium-like atom, then the repulsion of the electrons makes it impossible to solve the problem analytically. To orient ourselves and to understand the effect of the repulsion, let us provisionally make some simplifying assumptions. Since an electron can not be localized well, we can suppose that its charge fills a ball of radius R homogeneously. Such an electronic cloud would produce an electrostatic potential

$$V(r) = \begin{cases} -\frac{3e}{2R} + \frac{e}{2R} \left(\frac{r}{R}\right)^2, & r \leq R \\ -\frac{e}{r}, & r \geq R \end{cases} \quad (1.2.6)$$

(Figure 1). The potential energy of one electron and the nucleus is consequently $ZeV(0) = -3Ze^2/2R$. We can gauge the kinetic energy by reference to the hydrogen atom, for which the following rule of thumb leads to the correct ground-state energy: An electron cloud having potential energy $-Ze^2/r_b$ requires a kinetic energy $\hbar^2/2mr_b^2$. We set the kinetic energy equal to $9\hbar^2/8mR^2$, since $R = 3r_b/2$ provides the same amount of potential energy.

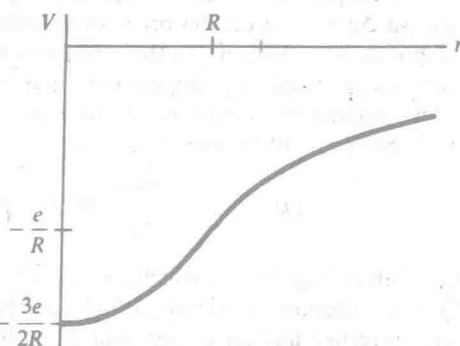
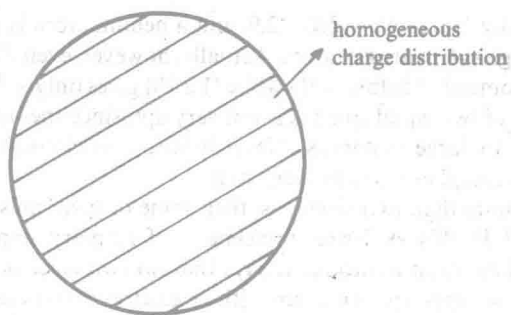


Figure 1 The potential of a homogeneous charge distribution.

If the second electron is also a homogeneously charged sphere coinciding with the first one, then the electronic repulsion is

$$-\frac{3}{4\pi R^3} 4\pi e^2 \int_0^R r^2 dr V(r) = \frac{6e^2}{5R}. \quad (1.2.7)$$

Therefore we obtain the ratio

$$\frac{|\text{Attraction of the electrons to the nucleus}|}{\text{Repulsion of the electrons}} = \frac{2 \cdot (3Ze^2/2R)}{6e^2/5R} = \frac{5Z}{2}, \quad (1.2.8)$$

and thus the total energy is

$$\begin{aligned} E(R) &= \text{kinetic energy} + \text{nuclear attraction} + \text{electronic repulsion} \\ &= 2 \cdot \frac{9\hbar^2}{8mR^2} - 2 \cdot \frac{3Ze^2}{2R} \left(1 - \frac{2}{5Z}\right). \end{aligned} \quad (1.2.9)$$

This has its minimum at the value $R = R_{\min} = R_H/(Z - \frac{2}{5})$, where

$$E(R_{\min}) = -Ry \cdot 2Z^2 \left(1 - \frac{2}{5Z}\right)^2. \quad (1.2.10)$$

If $Z = 2$, then $R_{\min} = 5R_H/8$, and the energy has the value $-2Ry \cdot \frac{64}{25} = -2Ry \cdot 2.56$. For such a primitive estimate, this comes impressively near to

the experimentally measured $-2Ry \cdot 2.9$, and a helium atom is indeed only about half as large as a hydrogen atom. Actually, however, even if $Z = 1$ (H^-) the energy lies somewhat below $-Ry$ while (1.2.10) gives only $-\frac{18}{25}Ry$. In this case the picture of two equal spheres is not very apt, since the outer electron will travel out to large distances. Nevertheless, nonrelativistic quantum mechanics describes these systems very well.

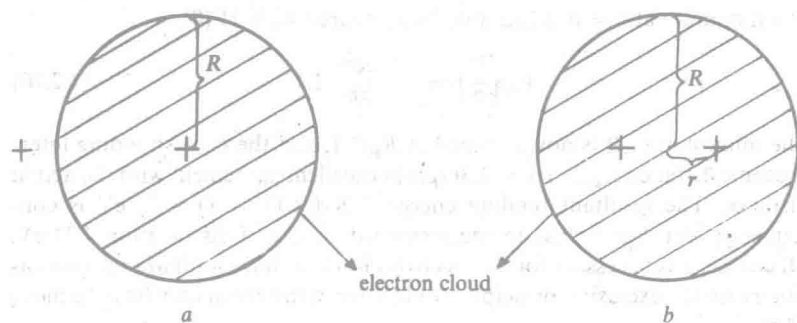
If there are more than two electrons, then some of them must have spins in parallel, and **Pauli's exclusion principle** is of primary importance for the spatial configuration of atoms; it says that no two electrons may have the same position, spin, etc. An atom with N electrons and radius R has a volume of about R^3/N per particle. Electrons insist on private living quarters of this volume, so Δq will be on the order of the distance to the nearest neighbor, which is $R/N^{1/3}$. This makes the zero-point energy of an electron $\approx \hbar^2 N^{2/3}/2mR^2$, as a rough approximation, and its potential energy $\approx -e^2 Z/R$. The minimum energy is attained at $R_{\min} = \hbar^2 N^{2/3}/me^2 Z$, making the total energy of all the electrons

$$E(R_{\min}) = -\frac{e^4 Z^2 m}{2\hbar^2} N^{1/3}. \quad (1.2.11)$$

The value R_{\min} is an average radius, which goes as $N^{-1/3}$ for $N = Z$, making $E \sim N^{7/3}$. Yet the outermost electrons, which are the important ones for chemistry, see a screened nuclear charge, and the radii of their orbitals are $\approx \hbar^2/me^2$. Strangely enough, it is not yet known whether the Schrödinger equation predicts that these radii expand, contract, or remain constant as $Z \rightarrow \infty$. Their contribution of about 10 eV to the total energy (1.2.11), on the order of MeV for $Z \sim 100$, is rather slight, however.

Chemical forces also arise from an energetically optimal compromise between electrostatic and zero-point energies. History has saddled us with a misleading phrase for this, **exchange forces**. Let us now consider the simplest molecule, H_2^+ , that is, a system of two protons and one electron. There is clearly a negative potential energy if the electron sits right in the middle of the line between the two protons. But is it possible for the electron's potential energy to be sufficiently negative to make the total energy less than that of H, or would its wave-function be too narrow, giving it an excessive zero-point energy? To be more quantitative about this question, let us again imagine that the electron is a homogeneously charged sphere with the potential (1.2.6). The radius R is chosen the same as for H, so there is no difference between this zero-point energy and that of hydrogen. If, as with H, we put one proton at the center of the cloud (Figure 2a), the potential energy is $eV(0)$. Taking the Coulombic repulsion of the protons into account, we note that the second proton feels no potential as long as it is outside the cloud, but when it comes to within a distance $r < R$ its energy increases, because

$$V(0) + V(r) + \frac{e^2}{r} \geq V(0). \quad (1.2.12)$$

Figure 2 Two electron distributions assumed for H_2^+ .

Hence there is no binding. However, if the two protons are placed diametrically across the center of the electron cloud, at radius r (Figure 2b), then the total potential energy

$$2V(r) + \frac{e^2}{2r} = -\frac{3e^2}{R} + \left(\frac{e^2}{R}\right)\left(\frac{r}{R}\right)^2 + \frac{e^2}{2r} \quad (1.2.13)$$

has the minimum

$$-\frac{3e^2}{2R} [2 - 2^{-1/3}] = -\frac{3e^2}{2R} \cdot 1.2 \quad (1.2.14)$$

at $r = 2^{-2/3} \cdot R$. This is more negative than $V(0)$, the energy with one proton outside the sphere, by a factor 1.2, and so we expect H_2^+ to be bound. If the total energy is now minimized with respect to R , then $R_{\min} = R_{\text{H}}/1.2$ and $E(R_{\min}) = -(1.2)^2 \text{ Ry}$. The separation $2r$ of the protons at the minimum is $2^{1/3} R_{\min} = 1.57 r_b$, which is significantly smaller than the experimental value $2r_b$. The binding energy $((1.2)^2 - 1) \text{ Ry}$ also amounts to more than twice the measured value, so the simple picture is not very accurate.

Finally, consider the molecule H_2 , again assuming that the H atoms are spheres. If they do not overlap, then the electrostatic energy is twice that of a single H atom, and the two separate atoms exert no force on each other. As the spheres are pushed together, the energy first decreases, since the repulsion of the electrons is reduced (the energy of two uniformly charged spheres at a distance $r < 2R$ is less than e^2/r), while the other contributions to the energy remain unchanged. In order to find out how much energy can be gained by making the spheres overlap, let us superpose them and place the protons diametrically across their center at a distance r . As with the helium atom, the electronic repulsion is $6e^2/5r$, and hence the total potential energy is

$$V_{\text{H}_2}(r) = -\frac{6e^2}{R} + 2\frac{e^2 r^2}{R^3} + \frac{e^2}{2r} + \frac{6e^2}{5R} \quad (1.2.15)$$

The minimum at $r = R/2$ can now be compared with $2V(0)$:

$$V_{H_2}\left(\frac{R}{2}\right) = -2 \frac{3e^2}{2R} \cdot 1.1. \quad (1.2.16)$$

The minimum in R is now attained at $R_H/1.1$, and the corresponding interprotonic distance $3r_b/2 \cdot 1.1 = 1.36r_b$ is in excellent agreement with the actual distance. The resultant binding energy $2 \text{ Ry}((1.1)^2 - 1) \simeq 5.7 \text{ eV}$ is consequently also fairly close to the measured energy of dissociation 4.74 eV . Of course, it is necessary for the electrons in H_2 to have antiparallel spins, as otherwise the exclusion principle would restrict the room they have to move about in.

One lesson of these rough arguments is that delicate questions like that of stability depend on small energy differences. It will require highly polished calculational techniques to reach definitive conclusions.