

The Illusion of Precision in Quantum Mechanics

Claes Johnson¹

¹KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden ,
claesjohnson@gmail.com

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Abstract

A fitted model is exact in the aspect it was fitted to. That exactness is automatic and carries no information, because it was arranged; what a model does *outside* its fit is the only thing that can fail, and therefore the only thing that is evidence. Textbook quantum mechanics begins by reporting the hydrogen ground state as -0.500000 and treating this as exact, then concludes that the Schrödinger equation is exact for any number of electrons and merely uncomputable. Both steps deserve examination. The figure -0.500000 mixes a prediction with a convention: the pattern $1/n^2$ is predicted, while the coefficient $\frac{1}{2}$ defines atomic units, and the bridge from atomic energy to measurable frequency is Planck's constant, itself fixed by the spectra it is then used to reproduce. The bound-state spectrum is thus the fitted aspect, and exactness there is free. The first genuinely unfitted predictions fail: applied correctly as a two-body problem, which it handles exactly, the equation reaches only 1.1×10^{-5} on the ground state, and it makes $2s$ and $2p$ degenerate against a measured splitting of 1058 MHz. It is the leading term of an expansion completed by Dirac and by quantum electrodynamics. The $3N$ -dimensional equation for N electrons is then a separate postulate, never solved without approximation beyond three or four electrons, so its exactness is supported only by extrapolation from a case where exactness is tautological. The electron's anomalous moment to twelve digits, usually offered in evidence, is a one-particle vacuum quantity of quantum electrodynamics and says nothing about it. We set against this a model of non-overlapping electron charge densities in three dimensions — equally a postulate, with no claim to exactness — whose energies, geometries and ionization energies come out within a few per cent from one electron to the ten thousand of a protein, parameter-free and computable. The comparison is not accuracy against inaccuracy, but a precision confined to few-electron systems against an accuracy that can be stated at every size.

1 The premise

The claim that organises every introduction to the subject is that the Schrödinger equation solves hydrogen exactly. Written for one electron about a fixed point charge,

$$-\frac{1}{2}\nabla^2\psi - \frac{1}{r}\psi = E\psi, \tag{1}$$

it has the ground state $E = -\frac{1}{2}$ in atomic units, which is 13.605693 eV, and a spectrum $E_n = -1/2n^2$ reproducing the Balmer series. The agreement was decisive in 1926 and remains the reason the equation is believed.

The question is what that agreement establishes. To answer it one has to ask where the two terms in (1) came from, because they did not come from the same place.

2 Where the form came from

The potential is not ad hoc. The term $-1/r$ is Coulomb's law, and it enters (1) already established. It was measured by Coulomb in 1785 on a torsion balance at macroscopic separations, in experiments that knew nothing of atoms or of spectra, and the inverse-square form has since been confirmed to extraordinary precision in settings entirely unrelated to the hydrogen atom. It arrives with no freedom: there is no exponent to select, no prefactor to tune, nothing in it adjusted to atomic measurements. Whatever fitting went into (1), the Coulomb term is not where it happened.

The kinetic term is. The operator $-\frac{1}{2}\nabla^2$ has no comparable standing. Nothing in electrostatics or in mechanics requires the quadratic form

$$T[\psi] = \frac{1}{2} \int |\nabla\psi|^2 dx, \quad (2)$$

and it was not derived from anything prior. Schrödinger reached it by analogy — with Hamilton–Jacobi theory and with de Broglie's relation — and an analogy is not a derivation. The decisive detail is what happened to the alternative: he wrote a relativistic wave equation first, found that its eigenvalues gave the wrong fine structure for hydrogen, and set it aside in favour of the non-relativistic form, which gave the right gross spectrum. The surviving operator is the one that produced the observed levels. It was selected *by* its spectrum.

So the two ingredients of the equation have opposite status. One carries independent empirical support obtained without reference to atoms. The other was chosen because its eigenvalues came out as the ones already on the table.

What was on the table. The pattern was known before the equation existed. Balmer wrote down his formula for the visible hydrogen lines in 1885 and Rydberg generalised it in 1888, both purely empirically: the lines go as differences of $1/n^2$. Equation (1) was accepted because it returns exactly this — which is to say, it reproduces the data that selected its form. The $1/n^2$ pattern is a consequence of the equation, but the equation is a consequence of the pattern.

The famous -0.500000 then has a second, separate issue: the digits are not an outcome at all. The coefficient $\frac{1}{2}$ in (2), and with it a ground state at exactly $-\frac{1}{2}$, is a statement about units — atomic units are defined so that this is the number. Converting it into something measurable needs a bridge from atomic energy to the energy of light, and that bridge is Planck's constant, through $\Delta E = h\nu$. But h — equivalently R_∞ , since the Hartree is $2R_\infty hc$ — is itself fixed by spectroscopy, and the hydrogen spectrum is among the measurements that fix it. The scale is read off the spectrum and then put back into it.

Taken together: the choice of (2) among the forms one might have written, and the constant connecting its eigenvalues to observed frequencies, were both settled by agreement with the hydrogen spectrum. In the narrow sense the equation has no adjustable parameter — given $\hbar$, m_e and e the ground state follows. In the sense that matters for the word *exact*, it is a model of simple form whose form and whose scale were selected to fit one body of data, and it is that body of data which is then presented as its triumph.

This is the point on which the whole question turns, and it is worth stating as a principle:

A fitted model is exact in the aspect it was fitted to.

That exactness is automatic. It carries no information, because it was arranged. The informative question is never how well a model reproduces what selected it, but what it does *outside* the fit — and the answer there is a prediction, which can fail.

3 Outside the fit

For hydrogen the fitted aspect is the bound-state spectrum: the $1/n^2$ pattern and, through h , its scale. Exactness there is free. The first genuinely unfitted predictions are close at hand, and the equation gets them wrong.

One candidate failure must be set aside first, because it is not the equation's. The nucleus moves, and (1) holds it fixed — but that is a shortcoming of how the equation has been *applied*, not of the equation. Written for two bodies it separates exactly into centre-of-mass and relative motion, and the relative part returns the hydrogenic spectrum with the reduced mass $\mu = m_e m_p / (m_e + m_p)$ in place of m_e , giving 13.598287 eV. That is the equation's own answer, and it is obtained exactly. The proton's motion is no defect of (1); charging it with one would repeat precisely the misattribution this article is about.

What remains cannot be dismissed that way. The residual against the measured 13.598435 eV [1] is

$$0.000147 \text{ eV}, \quad 1.1 \times 10^{-5} \text{ relative},$$

and this is a genuine deficiency: the relativistic and radiative physics the equation does not contain, supplied later by the Dirac equation and by quantum electrodynamics. Five significant figures, not infinitely many.

The spectrum fails more sharply, and qualitatively rather than numerically. Equation (1) makes $2s$ and $2p$ exactly degenerate. They are not: the splitting is 1057.845 MHz, the Lamb shift [2], whose discovery in 1947 initiated renormalised quantum electrodynamics. Here the equation does not return a slightly wrong number; it returns zero where there is an effect. Fine structure enters at order $\alpha^2 \approx 5 \times 10^{-5}$ of the binding energy and the Lamb shift at order $\alpha^3 \approx 4 \times 10^{-7}$; (1) contains neither.

So the equation said to be exact for hydrogen is the leading term of an expansion. It is exact in the aspect it was fitted to, and in the first two aspects it was not fitted to it fails — the second one qualitatively, requiring Dirac and then quantum electrodynamics to repair. That is the ordinary and respectable fate of a good model tested beyond its fit. It is not the record of an exact equation, and none of it is news to atomic physics. It is a correction to what the hydrogen case is taken to establish.

4 The step that is not justified

For N electrons the equation is written in $3N$ dimensions,

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i < j} \frac{1}{r_{ij}} \right] \Psi(x_1, \dots, x_N) = E \Psi, \quad (3)$$

with Ψ antisymmetric. This is a separate postulate. It is not derived from (1); it is (1) generalised by writing the same two ingredients once per electron and adding pairwise repulsion, and it carries two further components — antisymmetry and spin — that one-electron hydrogen never required.

The generalisation is natural and may well be right. What is not available is evidence that it is *exact*, and the reason is that nobody has solved it. Direct solution of (3) costs exponentially in N and is out of reach beyond three or four electrons. Every number the standard formalism produces for a real molecule comes from an approximation — a basis set, a functional, an active space, a truncated expansion — and the accuracy one can state depends on which approximation was chosen rather than on the equation.

So the claim “exact in principle, merely uncomputable” has an unusual structure. It cannot be tested, because testing it would require the computation that is said to be impossible. And the inductive support offered for it is the hydrogen case — where, by Section 2, the exactness is in the fitted aspect and therefore empty, and where, by Section 3, the first unfitted predictions fail and the spectrum is qualitatively wrong about a degeneracy. An extrapolation from a case that does not hold to cases that cannot be checked is not a strong position, however widely it is held.

5 The showcase, and what it shows

The claim examined here is usually made in the form Feynman gave it, and it is worth having in his words. Having quoted the electron’s magnetic moment as 1.00115965221 from experiment against 1.00115965246 from theory, he writes [3, ch. 1]:

At the present time I can proudly say that there is no significant difference between experiment and theory! . . . To give you a feeling for the accuracy of these numbers, it comes out something like this: If you were to measure the distance from Los Angeles to New York to this accuracy, it would be exact to the thickness of a human hair.

The figures have improved since: the moment is now measured to 0.13 parts per trillion [5] and agrees with the calculated series [6] at about one part in 10^{12} . The description of this as the most precisely tested prediction in science is fair; the inference usually drawn from it is not.

Note what Feynman is careful to say, and about what. His claim is about *quantum electrodynamics* — he names it in the same breath — and the number he chooses is a one-particle quantity. That is exactly the distinction this section turns on, and the canonical source for the precision claim already observes it.

The quantity is one-particle. It concerns a single electron’s interaction with the quantised electromagnetic vacuum, computed as a perturbative series in α within quantum electrodynamics. It involves no many-electron wavefunction, no antisymmetry among several electrons, no $3N$ -dimensional equation. It is evidence — overwhelming evidence — that QED describes the vacuum coupling of one charge. It is not evidence about (3), and offering it in support of the many-electron equation confuses two different theories with one Lagrangian between them.

Two further points are worth making precisely. The comparison requires α , and the most precise determinations of α now come either from a_e itself or from atom-recoil measurements whose results have at times disagreed at the level of the comparison [7, 8]; so part of the agreement is internal rather than independent. And the precision is a property of the observable, not of the theory’s reach: twelve digits on a vacuum quantity coexists with no ability to state an error bar on a hundred-electron molecule.

That last point is not a private complaint. Leggett, reviewing what has actually been tested, begins from the same observation [4, p. R415]:

Despite this enormous range of applications, however, there is a sense in which we can say that the region of the whole parameter space over which the validity of QM has been directly tested is still rather modest.

His concern is length scale and the size of superposed objects rather than electron count, but the structure of the argument is the same one made here: a theory can be confirmed to many digits inside a narrow region and remain untested over most of the range in which it is nevertheless assumed.

6 A second generalisation: the continuum model

The hydrogen equation (1) does not determine its own extension to many electrons. Equation (3) is one way of extending it — promote the wavefunction to a function of $3N$ variables and impose antisymmetry — and Section 4 is the observation that this is a postulate rather than a consequence. If it is a postulate, it is not the only one available, and the natural question is what a different extension of the same hydrogen model looks like and how it fares.

We call the alternative examined here the *continuum model*, or RealQM. It keeps both ingredients of (1) unchanged — Coulomb interaction and the kinetic form (2) — and extends them without leaving three-dimensional space. Instead of one antisymmetric function of $3N$ variables, there are N electronic charge densities occupying *non-overlapping domains* in ordinary space, each contributing its own kinetic and potential energy, interacting through the Coulomb potential they jointly generate, and meeting with continuity of density and potential across free boundaries whose position the energy itself determines [11]. Exclusion is realised geometrically, by the domains not overlapping, rather than by antisymmetry in a high-dimensional space; there is no spin; Z is the only quantity supplied.

For one electron the two extensions coincide: with $N = 1$ there is a single domain, no exclusion condition to impose, and the continuum model *is* (1). Both are generalisations of the same hydrogen atom, agreeing exactly where that atom is all there is, and differing only in what they do with the second electron. That is what makes the comparison in Section 7 a comparison and not a change of subject.

Nothing argues that this is exact, and we do not claim it. It is a postulate, chosen for the same kind of reason (2) was chosen: it is the simplest generalisation of the two ingredients that remains three-dimensional, and it can be computed. Its predictions are therefore to be checked rather than deduced, and the checking has been done over a wide range:

- total atomic energies within 1–2% on average across the first three periods, worst case 4.5% at silicon, every atom solved the same way with nothing fitted [12];
- the two-electron systems He and H₂ within a few per cent and bracketing the exact energies, as set out below, with the H₂ bond length at 1.368 against 1.401, 2.3%;
- first ionization energies of the alkalis and second of the alkaline earths within 1.4% and 4% respectively, from one constant per column, against the measured radius of the ion that remains [13];
- the row lengths 2, 8, 8, 18, 18, 32, 32 and closure at all seven noble gases, from the pair and the octet with no $2n^2$ entering;
- hydrogen-bond geometry and secondary structure in polypeptides of up to 153 residues, carried with their electrons on a laptop.

The failures should be stated with the same directness. The H_2 *binding* energy comes out 58% high — which is the 8.6% error on the total divided by the bond energy being a seventh of it, not an independent defect, but 58% nonetheless. Ionization energies require a radius supplied from measured ionic radii, so that result is a correlation between two measured quantities and not a prediction from Z . Proton affinities come out with the wrong sign. Dispersion-bound systems are outside range. The model is not accurate in the sense the standard formalism is accurate for helium, and it will not become so.

Two electrons: two models, and a bracket

At $N = 2$ the construction can be closed in two ways, and both are instructive because they fail in opposite directions.

Split. The non-overlapping form. The two electrons occupy the two half-spaces either side of the plane bisecting the axis, meeting at a free interface across which the natural (Neumann) condition holds. Each electron feels the other’s potential and not its own, so the pair is counted once and self-repulsion is excluded by construction.

Hom. The overlapping form: both electrons carried by the *same* density over the whole domain — sitting on top of each other. Non-overlap is then abandoned and something must take its place, because a single blob of charge 2 and density 2ρ has Coulomb self-energy $\frac{1}{2} \iint (2\rho)(2\rho)/|x-y| = 2J$ with $J = \iint \rho\rho/|x-y|$, which counts the one pair present twice. Reducing the repulsion energy by a factor two restores the correct count, and the model is

$$E = 2(T + V_K) + J, \quad \left(-\frac{1}{2}\nabla^2 - K + P[\rho]\right)u = \varepsilon u, \quad (4)$$

each electron seeing the other’s unit charge through $P[\rho]$.

Both were computed in the same code, on the same five-rung mesh ladder, by axisymmetric reduction — which is exact here, since the domains and the kernel potential are all invariant about the axis, so nothing is discarded in passing to two dimensions. Two controls fix what the discretisation contributes: one electron on the same meshes gives -0.500179 for H and -2.001615 for He^+ , errors of 0.04% and 0.08%. And (4) has a known answer to be checked against — it is the Hartree functional, which for a closed two-electron shell coincides with Hartree–Fock — so the Hartree–Fock limits must come out, and they do: -2.86111 against -2.861680 for He and -1.13363 against -1.133630 for H_2 , to 0.02% and to all five figures. The errors reported below are therefore the models’ and not the mesh’s.

The exact energies lie between the two:

$$\begin{array}{ccccc} \text{He:} & \underbrace{-2.8611}_{\text{hom, +1.5\%}} & < & \underbrace{-2.903724}_{\text{exact}} & < & \underbrace{-3.0265}_{\text{split, -4.2\%}} \\ \text{H}_2 \ (R = 1.4) : & \underbrace{-1.1336}_{\text{hom, +3.5\%}} & < & \underbrace{-1.174476}_{\text{exact}} & < & \underbrace{-1.2750}_{\text{split, -8.6\%}} \end{array}$$

and the same bracket holds on the H_2 binding energy, where it is wider because the binding is a seventh of the total: 0.1333 for hom and 0.2747 for split, against 0.1745, which is 24% low and 57% high. Overlapping the densities and halving the repulsion under-binds; separating them completely over-binds. The truth sits between, which is what one would expect of two idealisations of the same interface.

Why split is the model. Only one of the two generalises. Beyond $N = 2$ the hom construction has no definite content: putting all N electrons in one density requires a rule for what replaces non-overlap, and no choice is canonical — a charge- N blob with the repulsion scaled by $(N-1)/N$ is one guess, and it has no shell structure whatever, every electron sitting in the same lowest state, so no atom past helium and no periodic table. Restoring distinct states requires them to be orthogonal, which is antisymmetry, which is (3) again. The split construction needs no such decision: N densities on N non-overlapping domains, every pair counted once by the $i \neq j$ rule, exactly as at $N = 2$. So hom is a bracketing device for two electrons, and split is the model for all N .

Why two electrons are representative

The few per cent above is not an artefact of a small system, and this is the point on which the whole comparison rests. It is the accuracy the model has everywhere. Across the first three periods the mean error on total atomic energies is 1–2% with a worst case of 4.5%; helium is 1.5% and H_2 3.5% on the hom side, 4.2% and 8.6% on the split side; ionization energies of the alkalis come within 1.4%; hydrogen-bond geometries and secondary structure in a 153-residue protein are right to a few per cent. One electron, two, eighteen, ten thousand — the figure does not move much.

It does not move because its source does not change with N . The error is in the treatment of the interface between two charge densities, and a system of ten thousand electrons has the same kind of interface as a system of two, merely more of them. Adding electrons multiplies the number of boundaries without altering what happens at any one of them, and the errors are of one sign and largely cancel in differences taken within a fixed composition — which is why geometries come out better than total energies.

This is the opposite of the behaviour in Section 7. There the accuracy is twenty digits at $N = 2$, obtained by methods built for $N = 2$, and at $N = 10$ there is no error bar to quote. Here it is a few per cent at $N = 2$ for the same reason that it is a few per cent at $N = 10^4$. A constant error can be measured, and a model with a measurable error can be held to account at any size; an error that is unquantifiable past three electrons cannot be, however small it is where it can be evaluated.

7 Where the equation can be solved

For an equation advertised as exact for every N , the question that decides what the advertisement is worth is: for which N has it been solved? Not approximated — solved, to an accuracy the equation itself controls.

The answer is two, three, and with effort four. Helium is known to some twenty digits [9] and H_2 to twelve [10], by explicitly correlated expansions in the interelectronic distances. These are not truncations of a general procedure that merely becomes expensive; they are constructions built for a handful of particles, and they do not continue.

Past that, (3) is not solved. It is projected onto a finite basis and the projection is solved instead. Full configuration interaction reaches of order ten electrons in a basis too small to be the answer, at a cost that grows factorially, and the remaining error is the basis's rather than the equation's — not quantifiable against the exact solution, because the exact solution is what is missing. Beyond ten electrons the working methods are different theories: coupled-cluster at a chosen truncation, or density functionals carrying parameters fitted to measured data, the latter

having given up the wavefunction altogether. They are effective and they are what chemistry uses. Neither is the Schrödinger equation, and the agreement they achieve is evidence about them. For a protein there is no number of any kind.

There is a further turn to this, and it bears on how the per-cent figures of Section 6 should be read. The numbers a competing model is scored against are themselves largely computed. The -2.903724 for helium is not a measurement: it is the solution of the nonrelativistic Schrödinger equation at infinite nuclear mass, obtained by a purpose-built expansion — the equation under test, supplying its own benchmark. What is measured is the two ionization energies, and summing NIST’s values gives -2.903386 Ha; the remaining 0.00034 Ha is *removed by calculation*, being the relativistic, QED and nuclear-motion content that the measurement contains and the benchmark must not. Benchmark and measurement part company in the fourth decimal, and theory supplies the difference. For atoms generally the reference energies are explicit composites of experiment and *ab initio* calculation, computed outright past argon, because a nonrelativistic stationary-nucleus total electronic energy is not an observable — no instrument reads one. None of this impugns the composites, which are accurate. It does mean that “agrees with the exact value to n per cent” is a statement about distance from a construction that already contains the theory under test, and that bridging calculation to observation requires that same theory to supply the corrections.

So the equation is exact for all N and solvable for N of about three. The twenty digits are evidence about helium, which is specially tractable, and not about the formalism’s reach — and an exactness testable only where a bespoke method happens to exist, and replaced by fitted models everywhere else, has no content at the sizes chemistry and biology are made of.

Why the claim of universal agreement is nearly empty. This is the point at which the two halves of the standard position — *exact* and *uncomputable* — turn out to undercut one another, and it is worth stating bluntly. A disagreement with observation requires a prediction to disagree with. Past three or four electrons (3) yields no number at all; the numbers come from truncations and from fitted functionals. So for almost all of chemistry there is nothing for an experiment to contradict, and the celebrated record of never having been contradicted is, at those sizes, not a record of success but a record of *absence of exposure*.

The practice follows accordingly, and consistently. When a computed result does fail — dispersion missing, a barrier wrong, a spin state out of order — the failure is charged to the functional or to the basis and is repaired by adjusting those, never charged to the equation. That attribution is not dishonest; it is correct, because the equation was never evaluated and so cannot be what failed. But it means no observation can reach the equation at all. Uncomputability places it beyond refutation, and what is beyond refutation is equally beyond confirmation: the unbroken agreement is a property of the arrangement, not a finding about nature.

So the claim retains content exactly where computation is possible — hydrogen, helium, the one-particle vacuum quantity of Section 5 — which is also where the form was fitted and where the showcase sits. Everywhere else it is the empty statement that a theory which makes no checkable prediction has never been caught out. This is the same structure as the principle in Section 2, arrived at from the other side: there, exactness in the fitted aspect carried no information because it was arranged; here, agreement carries no information because nothing was risked.

8 What the comparison is about

The two models are both postulates. Both generalise Coulomb interaction and a chosen kinetic form to many electrons, in different ways, and neither generalisation is derived. They differ in what can be done with them.

One is exact in a limit nobody can compute, misses by 1.1×10^{-5} and by a whole splitting in the one case it solves exactly, achieves extraordinary precision for two and three electrons by methods that do not scale, and offers no error bar at all past ten. The other is exact nowhere, agrees with measurement to a few per cent, and does so at every size from one electron to ten thousand, in three dimensions, at linear cost, with nothing fitted.

The first is more accurate wherever it can be evaluated. The second is *answerable* wherever matter exists. A theory whose error is knowable and roughly constant can be held to account at every scale; a theory whose error is unknowable past four electrons can be held to account only there. Which property matters more depends on what one wants a model of matter for — and that is a question about scope, which is a legitimate scientific question, rather than a question about precision, which the twelve digits have already settled in a domain where nobody disputes them.

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