Making molecules into atoms

If the hydrogen molecule is two protons and one electron, how should it resemble the helium atom, which has one proton and two electrons?

THE hydrogen molecule-ion is of course the simplest molecule of all, which is no doubt why it has featured in elementary textbooks of quantum mechanics since virtually the beginning. Having dealt with the hydrogen atom, and shown that wave mechanics or some other calculating scheme can be made to work, textbook writers are naturally eager to show that the scheme will also work for molecules.

To be fair, the example of the hydrogen molecule-ion is as instructive as anybody could ask. One distinctive feature of this simple system is that it is a three-body problem which can no more be exactly solved in quantum than in classical mechanics. Another is that two of the three particles have equal mass. So, it may be asked, to what extent does the familiar treatment of the problem of the hydrogen molecule-ion apply to that other elementary three-body problem with two out of three masses equal, that of the helium atom?

This question has now been taken up by James M. Feagin of the California State University at Fullerton, and John S. Briggs from Freiburg University, West Germany (*Phys. Rev. Lett.* **57**, 984; 1986). On the face of things, it is a wrong-headed question. The unthinking assumption of quantum chemistry is that the motions of massive atomic nuclei are necessarily slow compared with those of the electrons in a molecule, and so may be neglected while calculating the patterns of electron distribution. This is the Born–Oppenheimer approximation, whose validity is attested by the fact that electronic transitions usually yield spectral lines in the visible or ultraviolet while nuclear motions (vibrations) yield spectral lines in the infrared.

A little thought, however, will show that the truth is not quite as simple, and that there is an uncomfortable element of circularity in anything that pretends to be a complete treatment of even the hydrogen molecule-ion. Suppose, for example, that the objective is to calculate not simply the allowable electronic states but the vibrational and rotational energy levels as well. The Born–Oppenheimer approximation first requires the calculation of the electronic states, each of which then determines the potential in which the two nuclei vibrate. For each electronic state, there will be an infinity of vibrational states. And for each combination of electronic and vibrational states, there will be an infinity of rotational states.

What the elementary books on quan-

tum chemistry fail to explain is that empirical spectroscopic evidence that might test these calculations is thin. Moreover, such tests as there may be tend to disappoint the calculators. But nobody need feel ashamed, for the complete calculation of the hydrogen molecule-ion, rotations as well as vibrations, depends on a succession of manifestly false assumptions. So, too, must any attempt to calculate the properties of a helium atom by the techniques worked out for the simplest molecule ion. But if the numbers are precise, their patterns could be instructive.

This is the line that Feagin and Briggs have followed. The argument is impeccable. In the usual calculation of the helium atom (two electrons and a more massive nucleus held together by Coulomb forces), a decent starting point is to suppose that each electron moves as if in a hydrogen atom, possibly with a central electric charge different from one (hydrogen) or two (helium) but somewhere in between. Then, the recipe says, take products of these wave functions (one for each electron) as starting points, and find which linear combinations of these products best suit the case.

Obviously, if the inter-electron distance in a helium atom is to correspond with the inter-proton distance in the calculation of the hydrogen molecule-ion, there will be a sense in which electronic states of the helium atom correspond to vibrational states of the hydrogen molecule-ion. Similarly, rotational states of one problem will correspond to vibrational states of the other. But the numbers calculated for, say, energy-levels will be very different. Only the countable triple infinity of states, and their symmetries, will be recognizable.

Nobody should mistake what Feagin and Briggs have done for a way of calculating the properties of helium atoms (or even those of the negative ion of positronium, one positron and two electrons). But it is vividly illustrative of several intriguing problems, especially of the molecular orbital approach to molecular calculations.

There, as the textbooks explain, the classical treatment of the hydrogen molecule-ion begins by supposing that one of the protons is very distant from the other. Then, to a very good approximation, the state of the system is that in which the electron is attached to either one or the other of the two protons or, naturally,

is some linear combination of the two. By allowing the distance between the two protons to shrink gradually, it is then possible to enumerate (but not to calculate exactly) the energy states of the molecule-ion in which the two nuclei are not widely separated from each other. In the prehistory of the 1930s, in the hands of people such as R.S. Mulliken, arguments like these made possible the extension of spectroscopy from atoms to molecules.

Feagin and Briggs attempt something along these lines. They do not abandon the advantage of knowing that nuclei are more massive than electrons, and therefore relatively immobile, but rather suppose that one point in the triangular interaction (the helium nucleus) is fixed in space. The hierarchy of quantum numbers at which they arrive is a shuffled version of those arising in the usual calculation of the helium atom: first comes a number corresponding to states of inter-electronic separation (electronic vibrations relative to each other), then one determined by both interelectronic separation and that of the electronic centre of gravity from the nucleus (total angular momentum?) and, finally, one involving the full geometrical coordinates of the three particles.

The outcome is impressive. Simply by scaling previous results for the hydrogen molecule-ion to allow for the differences of mass and charge, Feagin and Briggs are able to produce curves which show the energy of states of the helium atom as a function of inter-electronic separation whose symmetry is also well-defined. The description may be unfamiliar; those elementary textbooks tend to assert that inter-electronic distances are meaningless, which is true only to the extent that the Born–Oppenheimer approximation gives greater meaning to the concept of inter-nuclear distances.

The more general implication of this arresting piece of work is that it emphasizes, yet again, that quantum mechanics is just as positivist in its methods as was classical mechanics before it. If you have an arbitrary mechanical system, it is a matter of free choice how coordinates are specified for its description. Broadly speaking, the choice does not matter. But prudent physicists try to find coordinates with physical meaning, coordinates corresponding to measurable quantities. Even more prudent people try several choices, knowing that one may illuminate another.

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