

## Perspective

# Finding the way through intermolecular forces. Perspective on “Permanent and induced molecular moments and long-range intermolecular forces”

**Buckingham AD (1967) Adv Chem Phys 12: 107–142**

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Received: 15 February 1999 / Accepted: 16 March 1999 / Published online: 9 September 1999

**Abstract.** This is an overview of the title paper by A.D. Buckingham and a description of its impact and of many of the developments that it fostered.

**Key words:** Intermolecular forces – Permanent moment interactions – Polarization – Weak and long-range interaction

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We almost all start learning chemistry from the standpoint of atoms being the stuff of matter, and molecules being the stable combinations of atoms we find and synthesize. Hence, molecular structure and bonding define chemistry. However, at another level, there is structure and bonding – weak bonding – of molecules aggregating, and thereby forming clusters, droplets, and condensed phases. Molecules (and atoms) can and do stick to each other without forming “chemical” bonds. In many ways, this is its own chemistry, with rules of structure, energetics, and dynamics that are different – with a different physical basis – from the rules we invoke for individual molecules and their reactions. The two are intertwined. Chemical bonding somehow affects properties that play a role in weak interaction, and the weak interaction of surrounding molecules can have a profound impact on chemical reactions. The path to our understanding of the chemistry associated with intermolecular interaction has been complicated and challenging. A key report in that path is one written by A.D. Buckingham for *Advances in Chemical Physics* [1], a report that appeared about two-thirds of the way through the century that is closing and a report that is still relevant for embarking on the study of intermolecular interaction phenomena.

The basic parts of chemical bonding, such as orbital and configuration mixing, are not the primary features of weak and long-range interaction. Some may disagree with that, but even they are likely to see weak interaction

as a juxtaposition of several elements. Thus, anyone seeking fundamental understanding of weak interaction and intermolecular forces at some point has to examine and weigh competing and offsetting contributions. Buckingham’s paper is an essential source for finding the way through this juxtaposition.

To establish the setting for David Buckingham’s guiding review, one might go back a number of decades to the first ideas of nonbonding interactions between atoms and molecules; however, a fine place to start is just 10 years before the title paper when Coulson looked with great interest at the water–water interaction. A short article by Coulson [2] on this work is one of the best of those I know in recognizing very early why we would someday need to analyze in detail the contributions to hydrogen bonding, or more generally to weak interaction. He started by saying, “The hydrogen bond plays a very conspicuous role in human life, for it is responsible for the adherence of dirt to our skin, the structure of proteins, the action of glues and adhesives, the rigidity of many synthetic polymers, such as the polyamides, and a good many other biological phenomena.” He concluded by foreshadowing, perhaps, current-day biomolecular simulations when he said that water “is so small that it can fit into quite small interstices between the chains in any multiple helix” and it can “lie between two helices, and be quite tightly bound to them.” The weak and long-range interactions between molecules could be profoundly important, though the coarse level of analysis of the time needed improvement.

From among the things Coulson discussed, there was plenty to examine in depth. Buckingham clearly saw what deserved a high level of attention in the physics of weak interaction; it was electrical effects. One might say that Coulson provided the “why” and Buckingham defined the “what” for the story that was unfolding. Another major step was taken by Morokuma [3], and by others, though with Morokuma’s ways taking the strongest hold and being developed the most extensively.

This step was the “how” – how to extract the pieces that make up weak interaction, with the source being the then new things known as *ab initio* electronic structure calculations. In the 1980s, work of Applequist [4] yielded the “machinery” for weak interaction through his brilliant structuring of electrical interaction analysis suited to extensive calculations and simulations. Hence, in roughly a quarter of a century, the time spanned by Refs. [1–4] insight and inspiration, fundamental understanding, and mathematical/computational technology had all come together to find a way through the tangle of competing effects that comprise intermolecular forces.

Buckingham’s work is crucial in the saga. He started his 1967 report [1] with the statement “There is now general agreement that the significant forces between atoms and molecules have an electric origin.” He was building a solid case for a consistently important role of electrical interaction, which he said consisted of the interactions of permanent moments and the interaction energy associated with distortion of the electronic structure due to a neighboring molecule’s permanent moments. He referred to the first as the electrostatic energy and the second as the induction energy. He included a third attractive force, dispersion, pointing out its connection with polarizabilities. These terms are widely used in just that way today.<sup>1</sup> His overall thesis was that “detailed knowledge of molecular charge distributions and polarizabilities is essential for an understanding of intermolecular forces.” The power and scope of this statement could only emerge over a few more decades as theoretical and computational techniques evolved that could really provide the detailed knowledge.

Buckingham’s paper [1] gives a collection of formulas and symmetry analyses for evaluating electrical interaction energies and electromagnetic scattering, including treatment of periodically varying fields and special pairs of interacting systems. At the least, a lasting impact of this enumeration is in showing such analysis to be straightforward and readily adaptable to diverse molecular systems; it was doable and workable. This also made clear that chemists needed to think about electrical interaction more completely than that of two interacting molecular dipoles. That report connects several of the other major, contemporaneous developments from Buckingham [5–11] that together pushed spectroscopic study toward determination of precise quadrupole moment values, the study of many other electrical response properties with their anisotropies and frequency dependence, and optical activity generally.

Another key feature of the review [1] was the detailed connection of intermolecular interaction with the quantum mechanics of electronic structure. Buckingham offered a perturbative approach, taking the interaction as the perturbing Hamiltonian, and thereby associating the elements that make up the interaction with specific

terms and specific orders of perturbation. This type of analysis of weak interaction has expanded significantly, reaching a high and fruitful level of sophistication via *ab initio* methodology [12].

In the last decade or so, *ab initio* methodology has made possible high quality determinations of electrical response properties, i.e., multipole moments, multipole polarizabilities, and multipole hyperpolarizabilities. This has opened the door to utilizing Buckingham’s electrical interaction ideas to the fullest. One product was the Buckingham–Fowler model [13] for weakly bound complexes. This combined hard-sphere repulsion with permanent charge field interaction energies for the essentially attractive part of the potential. The model has yielded very nice determinations overall for shapes and structures of many complexes [13–16]. This is where my interest enters the story, since one of our developments is a model called molecular mechanics for clusters. It incorporated electrical interaction in a way that was open-ended with respect to the order of hyperpolarization and multipole [17]. Simple dispersion and exchange repulsion energies are added to the electrical energies to yield the complete potential. We had concluded from using our implementation of Morokuma’s partitioning scheme that Buckingham’s 1967 review had exactly the right direction. Electrical interaction was a crucial element for many types of clusters and it was something that could be well determined from properties intrinsic to the interacting species. We used Applequist’s structure [4] to include polarization response, and we have found many times that, indeed, shapes and structures of clusters can be nicely determined, and also vibrational frequencies, certain transition moments, and property changes (dipole moments, nuclear quadrupole coupling constants, etc.).

The role of induction or polarization that Buckingham addressed [1] over 30 years ago is turning out to be every bit as important as anticipated. Drawing on work we have done for examples, we find electrical polarization effects account for an unexpected correlation among four experimentally measured quantities for a series of carbon monoxyme proteins, the <sup>13</sup>C and <sup>17</sup>O chemical shifts of the CO, the CO group’s stretching frequency, and the <sup>17</sup>O quadrupole coupling constant [18]. I think this fits what Coulson foresaw. We can achieve insight, in this case insight that aids structural analysis for these types of proteins, through simulation based on fundamental understanding of contributing effects in weak and long-range interaction, even intramolecular electrical interaction. In a recent analysis, very sizable medium effects in a representative segment of solid-state polyacetylene were found to be due to mutual polarization [19]. Clearly, the polarization or induction part of electrical interaction is proving to be a key aspect of nonbonding interaction, and this is why Buckingham’s 1967 review [1] has had a strong impact.

Other successful models for weak interaction exist and more continue to appear, often with different application objectives and different ways of assembling and weighting components of intermolecular interaction. More and more, a foundational element for modeling

<sup>1</sup>Sometimes polarization energy is used for induction energy to avoid confusion with induction of current by a magnetic source. Also, permanent charge field interaction energy is sometimes used instead of electrostatic energy, reserving electrostatics for use in a collective sense that covers everything not varying in time, including polarization. Normally, usage is clear from the context.

efforts is electrical interaction. As well, simpler models such as those for molecular mechanics and molecular dynamics simulations are often being improved through more complete electrical analysis, such as incorporation of polarization effects.

Where are we heading as we enter the next millenium? Ten to fifteen years ago, we could study intermolecular interaction quite accurately and in detail with ab initio methods, but usually for systems with only two molecules – two small molecules. With the tremendous advances in computer technology and ab initio methods since then, what could be done for two small molecules can be done for tens of molecules now. Hence, models that were essential for, say, trimers and tetramers are being supplanted, and one might conclude that all this physical insight developed for weak interaction will have diminishing practical value. I do not share that conclusion. Instead, I see the expansion of the problems tackled by ab initio methods as being matched by an expansion in the scale of problems where detailed interaction modeling is invoked. For instance, where continuum modeling of solvents might have been the only manageable calculational route for condensed-phase simulations of reactions, explicit representation of individual solvent molecules is now tractable by many different means. In this way, I expect that Buckingham's ideas about the significant role of electrical interaction will broaden into the problems of proteins and water, of polymers, and maybe even as Coulson also thought, of glues and adhesives. Greater detail and more complete analysis have become possible through our more complete picture of intermolecular forces, and that offers more significant applications than we have yet seen.

*Acknowledgements.* Writing this report brings to mind the infectious enthusiasm for small complexes coming from W.H. Flygare and his group during my first years on the faculty at the University of Illinois. Bill was wonderfully supportive and inspiring for me, offering good guidance that included the important suggestion to look into a number of Buckingham's papers.

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