Published in final edited form as:

J Comput Chem. 2014 June 5; 35(15): 1159–1164. doi:10.1002/jcc.23612.

Transferable Pseudo-Classical Electrons for Aufbau of Atomic Ions

Solen Ekesan¹, Seyit Kale^{2,†}, and Judith Herzfeld^{1,*}

¹Department of Chemistry, Brandeis University, Waltham, MA 02454-9110, USA

²Graduate Program in Biophysics and Structural Biology, Brandeis University, Waltham, MA 02454-9110, USA

Abstract

Generalizing the LEWIS reactive force field from electron pairs to single electrons, we present LEWIS• in which explicit valence electrons interact with each other and with nuclear cores via pairwise interactions. The valence electrons are independently mobile particles, following classical equations of motion according to potentials modified from Coulombic as required to capture quantum characteristics. As proof of principle, the aufbau of atomic ions is described for diverse main group elements from the first three rows of the periodic table, using a single potential for interactions between electrons of like spin and another for electrons of unlike spin. The electrons of each spin are found to distribute themselves in a fashion akin to the major lobes of the hybrid atomic orbitals, suggesting a pointillist description of the electron density. The broader validity of the LEWIS• force field is illustrated by predicting the vibrational frequencies of diatomic and triatomic hydrogen species.

Keywords

LEWIS; DFT; reactive force field; explicit electrons; ionization energy; electron affinity; spin excitation; oxidation states

INTRODUCTION

Although molecular structure, dynamics and reactivity are all governed by electrons, they are generally modeled quite differently. Molecular structure and dynamics are usually efficiently simulated by molecular mechanics in which the effect of electrons are implicit in the partial charges on, and the multi-body interactions among, unitary atoms (e.g., OPLS,¹ CHARMM² and AMBER³). Although such implicit-electron descriptions have been extended to the realm of reactions in force fields that continuously recalculate bond orders on the fly (e.g., ReaxFF⁴ and REBO^{5,6}), molecular reactivity is more commonly modeled with explicit electrons described by computationally demanding quantum mechanics.

*herzfeld@brandeis.edu.

†Current address: James Franck Institute, University of Chicago, Chicago, IL 60637

Supporting information: Details of the fits to the training sets, the derivation of vibrational frequencies, and the minimum energy structures of boron, fluorine and aluminum species are reported in supporting information.

Recently, greater computational efficiency has been sought by developing force fields for explicit electrons. The problem is to determine what forms the interaction potentials should take. The well-established potentials of the implicit-electron force fields (i.e., harmonics for bonds and bond angles, sinusoids for torsion angles, and Lennard-Jones for intermolecular interactions) provide no guidance. In eFF,⁷ the potential forms for explicit electrons were derived by making the severe approximation that each electron inhabits a Gaussian orbital.

While a heuristic approach to force fields is time consuming, it has the chance of providing a better set of potentials. The LEWIS force field^{8,9} takes this tack and also simplifies the problem by making only the valence electrons explicit and modeling them in pairs. For water, LEWIS provides an excellent description of cluster structures,⁸ the condensed phase,⁹ and proton defect solvation and dynamics.¹⁰ In the last case, it offered a new perspective on discrepancies in results obtained with different approximations of density functional theory (DFT). LEWIS also holds promise for describing acid- and base-catalyzed reactions of molecules with integer bond order. However, electron pairs are intrinsically incapable of describing free radicals or fractional bond order. The importance of these species calls for modeling at the single electron level.

With this motivation, we introduce LEWIS• (read: *Lewis-dot*), which differs from LEWIS in modeling the valence electrons singly, with spin characteristics and variable cloud size. It continues to differ from eFF in its heuristic approach to the force fields and in its implicit treatment of core electrons. As a first step, we endeavor to describe the aufbau of atomic ions. As proof of principle, we show that the ground and spin-excited states of the atomic ions of five elements from distant points in the first three rows of the periodic table can all be described with just one, context-independent set of pairwise interactions between electrons. By way of further validation, we also show that these interactions provide a good description of the vibration modes of H₂, H₂⁺ and H₃⁺.

LEWIS•

Particle Types

The particles in the model consist of positively charged atomic cores (subsuming the nucleus and any core electrons) and negatively charged valence electrons. The atomic cores (*X*) bear charges corresponding to their implicit constituents. Thus, for example, the charge of the hydrogen core is $q_H = +1$ and the chlorine core is $q_{Cl} = +7$.

The electrons are independently mobile, fully interchangeable, *pseudo-classical* particles. They are “*classical*” in the sense that they have coordinates that evolve in response to interactions with other particles and “*pseudo*” in the sense that the interactions are modified from the classical to take quantum behavior implicitly into account. The latter requires two types of electron particles, both with charge $q_e = -1$, but with opposite spins. Transferability also requires that each electron have a fourth coordinate that expresses variation in spread, envisioned as a cloud diameter, d , with corresponding quantum kinetic energy.

Particle Interactions

For efficiency, the interactions between all types of particles are strictly pairwise. Each particle is governed by the same potentials regardless of the environment. The spin description is taken into account by distinct pair potentials for interactions between electrons of like spin ($ee(l)$) and unlike spin ($ee(u)$). Our only other requirements are that the pair potentials be Coulombic at long distances and smoothly differentiable everywhere. The former is necessary for an accurate treatment of charges and the latter is important for energy conservation in long simulations. Even within these constraints, the range of possible functional forms is daunting. However, the effort is well repaid when it finds a high quality, efficient force field.

Training Sets

Since LEWIS• involves more particle types and particle degrees of freedom than LEWIS, it is challenging to gather an adequate training set for the pair potentials. The ideal set offers the maximum number of data points per particle type. This suggests single atom phenomena. Just three particle species (the two types of electron and the core of X) with three corresponding pair potentials ($U_{ee(l)}$, $U_{ee(u)}$) and element specific U_{eX} , are required to describe all the spin configurations of all the atomic ions of any one element X, in accord with Hund's rules. These are summarized in Table 1. For each spin configuration, we choose the quantum state with lowest energy for training. We include stable $\alpha 5$ configurations even though we don't expect LEWIS• to do a good job of describing electrons populating two shells. The intent is simply to assure that the energies of these species are sufficiently high that they don't appear inappropriately in future simulations.

To provide a solid foundation for electron transferability, we include two elements in the training set used to optimize the electron interactions $U_{ee(l)}$ and $U_{ee(u)}$. For this "primary training set" we choose chlorine from the far right of the third row and hydrogen from the first row. Chlorine has the advantage of including all possible s and p configurations within the third shell, which provides huge amount of data. To extend the primary training set to the first row, we wish to include hydrogen. On the other hand, since the ionization states of the hydrogen atom alone do not provide enough data for U_{eH} , we include properties of multi-atomic hydrogen species, with the assumption that the repulsions between protons are purely Coulombic, as they were in LEWIS⁹. The properties include energies and bond lengths for three stable multi-atomic hydrogen species and lower bounds of energies for four unstable multi-atomic hydrogen species. The quality of the description of elements as different as hydrogen and chlorine with just one set of electron-electron potentials provides the first test of electron transferability.

A further test of electron transferability is the effectiveness of the $U_{ee(l)}$ and $U_{ee(u)}$ pair potentials derived from chlorine and hydrogen in describing other elements. As these electron-electron potentials are applied unchanged to any element X, the data for each element X constitute a "secondary training set" used only to obtain the corresponding U_{eX} .

Form Search and Parameter Optimization

Knowledge-based trials of each set of potential forms require optimizing its parameters. Our objective function is a weighted sum of the absolute percent deviation from the experimental values in the training set. Minimizing the value of the objective function actually requires another layer of optimization: for each set of potential parameters it is necessary to find the minimum energy structure for each species in the training set before the objective function can be evaluated. The potential parameters were optimized using the differential evolution (DE) algorithm,¹¹ with the strategy DE/rand/1/exp. Our DE parameters were CR=1.0, F=0.5, and NP=3D, where D is the number of parameters optimized. Minimum energy structures were found using Monte Carlo (MC) simulations¹² at 1 K, long enough to be confident that the minimum has been reached.

The weights in the objective function were assigned according to anticipated importance for future simulations of reactions. The highest weights were given to the electron affinities and first ionization energies. The lowest weights were given to the energies of the spin excitations, which often represent only the bottom of a manifold. But high priority was given to getting both the correct orders of the spin-excitations and the instabilities of the multi-atomic hydrogen species.

RESULTS

Fitting the Primary Training Set: electron-electron and electron-core interactions

The total potential energy of any species includes single-electron and two-particle terms:

$$U_{Total} = \sum_{electrons} U_i + \sum_{all\ particles} U_{ij} \quad (1)$$

The single-electron term, U_i , corresponds to the quantum kinetic energy

$$U_i = \frac{3\hbar^2}{2m_e d_i^2} \quad (2)$$

based on the electron mass, m_e , and cloud diameter, d_i . The pair potentials, U_{ij} , in the present work are of four types: $U_{ee(u)}$, $U_{ee(l)}$, $U_{eX} = U_{Xe}$, and U_{HH} . As indicated above, we assume a simple Coulombic interaction between protons

$$U_{HH} = \frac{q_H^2}{r_{ij}} \quad (3)$$

where r_{ij} is the distance between hydrogen cores i and j .

All other pair interactions are the result of an onerous search through various functional forms. The effect of the diffuse distributions of the electrons is to soften their Coulomb interactions at short distances. As in LEWIS, the forms that provide suitable softening with sufficient flexibility are inverse roots of polynomials:

$$U_{eX} = \frac{q_e q_X}{\left(r_{ij}^8 + \kappa_{eX6}^2 d_{eff}^2 r_{ij}^6 + \kappa_{eX4}^4 d_{eff}^4 r_{ij}^4 + \kappa_{eX2}^6 d_{eff}^6 r_{ij}^2 + d_{eff}^8 \right)^{1/8}} \quad (4)$$

where

$$d_{eff} = \sigma_{eX} d_e + \rho_{eX} \quad (5)$$

and σ_{eX} scales the electron cloud diameter used for the kinetic energy and ρ_{eX} represents the extent of the core electrons implicit in X. Similarly for the interactions between electrons with unlike spin:

$$U_{ee(u)} = \frac{q_e^2}{\left(r_{ij}^8 + \kappa_{ee2}^6 d_{eff}^6 r_{ij}^2 + d_{eff}^8 \right)^{1/8}} \quad (6)$$

where

$$d_{eff} = \sigma_{ee} \sqrt{d_i^2 + d_j^2} \quad (7)$$

The interactions between electrons of like spin require an additional term reflecting Pauli exclusion. A damped oscillator form changes sign and vanishes with distance, just as the integrand of the exchange integral does in quantum calculations. Thus, we choose

$$U_{ee(l)} = U_{ee(u)} + q_e^2 \frac{\chi_{ee}}{d_{eff}^2} \cos \left(\tau_{ee1} \pi \left(\frac{r_{ij}}{d_{eff}} \right)^4 \right) \exp \left(-\tau_{ee2} \left(\frac{r_{ij}}{d_{eff}} \right)^2 \right) \quad (8)$$

where χ_{ee} scales the magnitude, τ_{ee1} determines where the sign changes, and τ_{ee2} controls the damping.

Transferability lies in having one $U_{ee(u)}$ (specified by 2 parameters) and one $U_{ee(l)}$ (specified by 3 more parameters) that will work with *all* elements. The question is with which element(s) to train these. Each element requires its own U_{eX} (specified by another 5 parameters, including the 2 in d_{eff}). Thus, for a lone element X, the number of parameters to be determined becomes 10. Given its ubiquity in aqueous and organic systems, hydrogen is a high priority for a force field. However, since none of the stable hydrogen species has more than one electron of each spin, it is not suitable on its own for training $U_{ee(l)}$. On the other hand, chlorine alone has enough data (the 14 energies shown in Figure 2) to determine all 10 parameters in $U_{ee(u)}$, $U_{ee(l)}$, and U_{eCl} . However, $U_{ee(l)}$ and $U_{ee(u)}$ potentials based on chlorine alone, proved non-transferable (i.e., they did not give satisfactory results for hydrogen). Combining the hydrogen and chlorine species together provided a rich primary training set, with 26 data to train a total of just 15 potential parameters for the two elements (5 for the transferable ee repulsions, 5 for the eH attractions, and 5 for the eCl attractions).

The resulting pair potentials are summarized in Figure 1 and Table 2. Consistent with our physical picture, $\rho_H=0$ reflects the absence of core electrons around the proton.

Figure 2a and Table 3 show the quality of the fit to the primary training set. Figure 2a shows that Hund's Rule (the order of all the spin excitations) is replicated and the energies of greatest importance are fit quantitatively. The main problem, as anticipated, is with spin excitations that elevate an electron to the next shell, i.e., the second spin excitation of Cl^+ (triangle and asterisk for the species with 6 electrons) and the first spin excitation of Cl (square and cross for the species with 7 electrons). This type of excitation can be imagined as a partial ionization, with an experimental value that fits between the two flanking ionization energies. It remains that LEWIS• describes the orders of spin excitations correctly in two very different elements, which is non-trivial for a single, context-independent set of pair potentials for interactions between electrons with like and unlike spins.

The first two sections of Table 3 show that LEWIS• also provides good reaction energies and the correct order of bond lengths for the hydrogen species. Better bond lengths could be obtained by increasing their weights in the fit, but H_3 and H_4 were inappropriately stable under the resulting potentials and this is a more serious defect in a reactive force field than underestimated bond lengths.

The minimum energy structures that gave the results in Figure 2a and Table 3 are shown in Figure 3 for the monoatomic chlorine species, and in Figure 4 for the multi-atomic hydrogen species. All the structures show that electrons of like spin avoid each other in the expected symmetries. Overall the electron cloud diameters are similar within a species and tend to expand with increasing numbers of valence electrons.

Fitting the Secondary Training set: electron-core interactions

As a more general test of the transferability, we applied the $U_{ee(l)}$ and $U_{ee(u)}$ potentials derived from hydrogen and chlorine data to several elements in the first three rows of the periodic table that have enough ionization states to determine the 5 parameters of the corresponding U_{eX} , assuming that the form of U_{eX} is invariant. To capture extremes, we choose boron and fluorine in the second row and aluminum in the third row. Figure 2b shows that, with only the values of the U_{eX} parameters varied from one element to another, the fit to the secondary training set is similar to the fit to the primary training set. The structures of species in the secondary set (Figures S3–S5) are consistent with the chlorine structures. For all the elements, the symmetries of the electron arrangements are similar among all instances of each spin configuration and the structures differ only by the electron-core distances and the sizes of the electron clouds.

Predictions

As a further test of the capabilities of LEWIS•, we reached beyond the training sets to calculate the vibrational frequencies of the di- and triatomic hydrogen species. The second panel of Table 3 shows the results obtained by evaluating the energies of constructs in the vicinity of the minimum energy structures (see Figures S1 and S2). The predicted diatomic frequencies agree with experimental values to within ~2%. The ratio of the frequencies for

the symmetric (A) and the doubly-degenerate, anti-symmetric (E) triatomic modes also agree well with experiment, but the absolute values are overestimated by ~50 %.

DISCUSSION

In 1961, Linnett¹³ argued that Lewis'¹⁴ octets should be regarded as a pair of quartets, rather than as a quartet of pairs. The LEWIS• structures in Figure 3 comport well with Linnett's concept. It can be seen that whenever four valence electrons of like spin are available they arrange tetrahedrally, while threesomes form equilateral triangles, and pairs are linearly disposed. In species with electrons of unlike spins, these geometries are intertwined and full pairing occurs in the octet (as in the case of Cl⁻).

Our main goals were both quantitative and qualitative. Accuracy in ionization energies is necessary to reasonably approximate the energetics of chemical reactions. At the same time, a correct description of the order of spin excitation is necessary to assure that free radical reactions produce the correct product. We found it extremely challenging to meet both of these goals simultaneously and the potential forms reported here are the only ones that we found that could do the job. Although the inverse root polynomials that we arrived at can

accurately approximate the error function form, $\left(\frac{1}{r}\right) \operatorname{erf}\left[\left(\frac{\sqrt{\pi}}{2}\right)\left(\frac{r}{d_{\text{eff}}}\right)\right]$ that is typically used for softened Coulombic interactions, the fit to the training set is optimal for potentials that are significantly different (as shown in Figure 1). Once found, the LEWIS• functional forms were consistently effective in fitting the data in our training set.

A non-trivial aspect of the LEWIS• force field is the crossover between $U_{ee(l)}$ and $U_{ee(u)}$ (Figure 1a). While crossing is necessary in order to conform to Hund's rules, it is non-trivial that a single crossover would be sufficient and that the location of that crossover would work equally well for elements in groups 3 and 7 and in rows 2 and 3.

How should we regard LEWIS•'s sidestep of the wave properties of electrons? One perspective is to consider the LEWIS• electrons as nothing more than mediators of the interactions that are employed in conventional atomistic force fields. Of course, electrons do in fact mediate those interactions, and explicitly representing that mediation allows the multi-body interactions governing bond angles and torsion angles in conventional force fields to be replaced by a larger number of pair interactions in LEWIS•.

Another perspective is to consider the LEWIS• model as a pointillist version of density functional theory (DFT). The theorems of DFT tell us that all we need to know about a molecule is contained in its ground state electron distribution¹⁵ and the LEWIS• structure can be regarded as a discretized approximation of that distribution. The functionals in DFT and the pair potentials in LEWIS• have in common that development requires intelligent trial and error with feedback from training sets, and neither has a route for systematic improvement.¹⁶ The difference is that LEWIS• is far less onerous computationally and, arguably, also more intuitive. On the other hand, DFT has had decades of work invested in improving the functionals while LEWIS• is brand new.

Compared to LEWIS, LEWIS• is more computationally costly because the number of particles representing the electrons is doubled and their variable cloud diameter adds another coordinate to each. Nevertheless, the efficiency of LEWIS• is comparable to that of LEWIS, which was shown to be orders of magnitude faster than DFT.⁹

CONCLUSIONS

The combination of the earlier successes of the LEWIS force field^{8–10} for electron pairs and this initial promising result for the LEWIS• force field for single electrons, suggests that the explicit valence electron construct with heuristic force fields can afford significant computational economies in descriptions of reactive systems without great sacrifices in accuracy. It is remarkable that strictly pairwise interactions can describe ionization and spin excitation energies of a specific atom, and even more remarkable that the potentials for electron-electron interactions are transferable between distant regions of the periodic table.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Research reported in this publication was supported by the National Institute of Biomedical Imaging and Bioengineering of the National Institutes of Health under award EB001035. Additional computational support was provided by the Brandeis HPC. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health.

References

1. Jorgensen WL, Maxwell DS, TiradoRives J. J Am Chem Soc. 1996; 118(45):11225–11236.
2. Brooks BR, Bruccoleri RE, Olafson BD, States DJ, Swaminathan S, Karplus M. J Comput Chem. 1983; 4(2):187–217.
3. Case DA, Cheatham TE, Darden T, Gohlke H, Luo R, Merz KM, Onufriev A, Simmerling C, Wang B, Woods RJ. J Comput Chem. 2005; 26(16):1668–1688. [PubMed: 16200636]
4. van Duin ACT, Dasgupta S, Lorant F, Goddard WA. J Phys Chem A. 2001; 105(41):9396–9409.
5. Brenner DW. Phys Rev B. 1990; 42(15):9458–9471.
6. Stuart SJ, Tutein AB, Harrison JA. J Chem Phys. 2000; 112(14):6472–6486.
7. Su JT, Goddard WA. Phys Rev Lett. 2007; 99(18):185003. [PubMed: 17995416]
8. Kale S, Herzfeld J, Dai S, Blank M. J Biol Phys. 2011; 38(1):49–60. [PubMed: 23277669]
9. Kale S, Herzfeld J. J Chem Phys. 2012; 136:084109. [PubMed: 22380034]
10. Kale S, Herzfeld J. Angew Chem Int Ed. 2012; 51(44):11029–11032.
11. Storn R, Price K. J Global Optim. 1997; 11(4):341–359.
12. Metropolis N, Ulam S. J Am Stat Assoc. 1949; 44(247):335–341. [PubMed: 18139350]
13. Linnett JW. J Am Chem Soc. 1961; 83(12):2643–2653.
14. Lewis GN. J Am Chem Soc. 1916; 38(4):762–785.
15. Hohenberg P, Kohn W. Phys Rev. 1964; 136(3B):B864–B871.
16. Burke K. J Chem Phys. 2012; 136(15):150901–150909. [PubMed: 22519306]
17. Herzberg G. Physical review letters. 1969; 23(19):1081–1083.
18. [Accessed February 1, 2013] CRC Handbook of Chemistry and Physics: 2013–2014. <http://www.hbcpnetbase.com>

19. Burt JA, Dunn JL, McEwan MJ, Sutton MM, Roche AE, Schiff HI. J Chem Phys. 1970; 52(12): 6062–6075.
20. Kolos W, Wolniewicz L. J Chem Phys. 1965; 43(7):2429–2441.
21. Schulz GJ. Rev Mod Phys. 1973; 45(3):423–486.
22. Meador WE. J Chem Phys. 1958; 29(6):1339–1345.
23. Barker RS, Snow RL, Eyring H. J Chem Phys. 1955; 23(9):1686–1689.
24. Symons MCR, Guy Woolley R. Phys Chem Chem Phys. 2000; 2(2):217–219.
25. Kolos W, Wolniewicz L. J Chem Phys. 1964; 41(12):3663–3673.
26. Kuchitsu, K. Structure of free polyatomic molecules. Springer; Berlin Heidelberg: 1998.
27. Bishop DM. J Chem Phys. 1970; 53(4):1541–1542.
28. Chang SY. J Chem Phys. 1972; 56(1):4–7.
29. Jacox, ME. Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules: in NIST Chemistry WebBook. In: Linstrom, PJ.; Mallard, WG., editors. NIST Standard Reference Database Number 69. National Institute of Standards and Technology; Gaithersburg MD, 20899: <http://webbook.nist.gov> [Accessed February 1, 2013]
30. Johnson, Russell D., III, editor. [Accessed February 1, 2013] NIST Computational Chemistry Comparison and Benchmark Database: NIST Standard Reference Database Number 101, Release 15b. Aug. 2011 <http://cccbdb.nist.gov/>
31. Kramida, A.; Ralchenko, Yu; Reader, J. NIST ASD Team. NIST Atomic Spectra Database: (version 5.0). National Institute of Standards and Technology; Gaithersburg, MD: 2012. [Online]. Available: <http://physics.nist.gov/asd> [Accessed February 1, 2013]

Figure 1.

Pair interactions (in $\text{\AA}^{-1}$) vs. distance (in $\text{\AA}$) for $d_{\text{eff}}=1.0$. (a) Repulsions between electrons with unlike and like spins, are shown in solid and dashed magenta lines, respectively. (b) Scaled core-electron attractions $U_{eX}/|q_X q_e|$, are shown for the elements of the primary training set: hydrogen (yellow) and chlorine (green). (c) Scaled core electron attractions, $U_{eX}/|q_X q_e|$, are shown for the elements of the secondary training set: boron (coral), fluorine (yellow-green) and aluminum (grey). For comparison, all panels show purely Coulombic interactions as dotted black lines and the corresponding error function form,

$$\left(\frac{1}{r}\right) \operatorname{erf}\left[\left(\frac{\sqrt{\pi}}{2}\right)r\right], \text{ as dashed black lines.}$$

Figure 2.

Ionization and spin excitation energies (in 10^3 kJ/mol) vs. the number of valence electrons in atoms and ions of the primary (a) and the secondary (b) training sets. The experimental values of the ionization energies^{18,30} (plotted at the half-integer points) and the first and second spin excitations³¹ (plotted at the integer points) are represented by circles, squares and triangles, respectively. The corresponding model values are represented by pluses, crosses and asterisks, respectively. (The pairs can be thought of targets and arrow tails.) (a) Primary training set: hydrogen (yellow) and chlorine (green). (b) Secondary training set: fluorine (yellow-green), boron (coral), and aluminum (grey). The values for the 6th and 7th ionization energies of chlorine, and 5–7th of fluorine which are off the scale of these graphs, can be found in Table S2.

Figure 3.

Minimum energy structures of the atomic ions of chlorine in oxidation states from +6 to -1, corresponding to 1–8 valence electrons. Spin states are in order of increasing energy from bottom to top. The chlorine core (*Cl*) is represented in green and is rendered transparent as necessary to show electrons concentric with the core. Electrons with spins α and β are rendered in magenta and light pink, respectively, with diameters scaled to the corresponding cloud diameter.

Figure 4.

Minimum energy structures of the multi-atomic hydrogen species. (Monoatomic species are not shown because the electrons are centered on the hydrogen core.) The hydrogen core (H) is represented in white and is rendered transparent as necessary to show electrons close to the core. Electrons with spins α and β are shown in magenta and light pink, respectively, with diameters rendered on the same scale as used in Figure 3.

Atomic ions included in primary and secondary training sets (when their experimental energies are available). The primary training set is used to train $U_{ee}(l)$ and $U_{ee}(u)$, as well as U_{eH} and U_{eCl} , whereas the secondary training sets are used to train only the corresponding U_{eX} .

Table 1

# valence electrons	Primary Set		Secondary Set			spin configurations in order of energy
	H	Cl	B	F	Al	
1	H	Cl ⁺⁶	B ⁺²	F ⁺⁶	Al ⁺²	a
2	H ⁻	Cl ⁺⁵	B ⁺	F ⁺⁵	Al ⁺	$a\beta < a2$
3		Cl ⁺⁴	B	F ⁺⁴	Al	$a2\beta < a3$
4		Cl ⁺³	B ⁻	F ⁺³	Al ⁻	$a3\beta < a2\beta2 < a4$
5		Cl ⁺²		F ⁺²		$a4\beta < a3\beta2 < a5$
6		Cl ⁺		F ⁺		$a4\beta2 < a3\beta3 < a5\beta$
7		Cl		F		$a4\beta3 < a5\beta2$
8		Cl ⁻		F ⁻		$a4\beta4$

Table 2

Values of the potential parameters.

Interaction	Parameters				
	$\chi/\text{\AA}$	τ_1	τ_2	κ_2	σ
ee(l)	32.6542	0.84436	1.92179		
ee(u)				1.07587	0.72939
eH	κ_6 1.53127	κ_4 0.79796	1.26299	0.57755	0
eCl	1.02169	0.08850	1.11480	0.44436	0.40190
eB	0.12533	0.88925	1.05987	0.49316	0.37975
eF	0.03665	0.33811	1.07203	0.59998	0.13875
eAl	0.13893	1.10126	1.10953	0.43475	0.60286

Table 3

Results for multi-atomic hydrogen species: bond lengths (in Å), reaction energies (in kJ/mol) and vibrational frequencies (in cm^{-1}). Whereas the reaction energies and bond lengths are fit as part of the primary training set, the vibrational frequencies are predicted by the resulting potentials.

	Exp	LEWIS•	% error
<i>Primary training set</i>			
Reaction energies			
$\text{H}_2 \rightarrow \text{H} + \text{H}$	432.06 ¹⁷	432.41	0.08
$\text{H}_2 \rightarrow \text{H}_2^+ + \text{e}^-$	1488.37 ¹⁸	1647.49	10.69
$\text{H}_3^+ \rightarrow \text{H}_2 + \text{H}^+$	424.54 ¹⁹	387.79	-8.66
H_2 (triplet) $\rightarrow \text{H} + \text{H}$	< 0 ²⁰	< 0	
$\text{H}_2^- \rightarrow \text{H}_2 + \text{e}^-$	< 0 ²¹	< 0	
$\text{H}_3 \rightarrow \text{H}_2 + \text{H}$	< 0 ²²	< 0	
$\text{H}_4 \rightarrow 2 \text{H}_2$	< 0 ²³	< 0	
Bond lengths			
H_2^+	1.05 ²⁴	0.90	-14.29
H_2	0.74 ²⁵	0.65	-12.16
H_3^+	0.88 ²⁶	0.74	-15.91
<i>Predictions</i>			
Vibrational frequencies			
H_2^+	2321.7 ^{27*}	2375.5	2.32
H_2	4401.213 ^{28*}	4273.288	-2.91
H_3^+ (A)	3178 ^{29*}	4827	52
H_3^+ (E)	2521 ^{29*}	3722, 3713	48, 47

* Results of high level quantum calculations, rather than experiment.