Transferability and the pair potential within the tight-binding bond model: an analytic study for hydrogen

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Abstract. A new analytic tight-binding (TB) pair potential and hopping integral are constructed for hydrogenic s orbitals, by coupling the Harris–Foulkes scheme with Anderson's chemical pseudopotential theory. The validity of using a fixed, transferable TB parametrization is studied and the limitations are found to be twofold. First, although qualitatively reproducing *ab initio* equilibrium binding energies and atomic separations for diatomic and bulk metallic simple cubic (SC) and face centred cubic (FCC) hydrogen, bulk moduli are globally poorly obtained. This reflects the strong environment dependence of the pair potential and hopping integral. Secondly, errors are incurred by keeping only pairwise terms in a cluster expansion of the exchange–correlation functional. They are found to be non-negligible for bulk systems, being about 25% of the total binding energy for the SC and FCC lattices.

1. Introduction

In order to perform large-scale atomistic simulations of complex systems such as surfaces, grain boundaries and amorphous solids, a model needs to be computationally economic, to be quantum-mechanically based and to incorporate intuitive concepts that lead to an improved understanding of physical trends and mechanisms. One such scheme, applicable to both semiconductors and transition metals, is the so-called tight-binding bond (TBB) model (Sutton *et al* 1988, Pettifor 1990 and references therein). Within this approach the binding energy of a collection of atoms is written in terms of a pairwise repulsive energy, a promotion energy and a covalent bond energy:

$$E_B = E_{rep} + E_{prom} + E_{bond}. \tag{1}$$

In the simplest minimal basis treatment the covalent bond energy is determined by solving a two-centre, orthogonal Slater–Koster Hamiltonian (Slater and Koster 1954). Interactions are usually assumed to be short-ranged and restricted to only first or first and second nearest neighbours.

In principle, the simple form of equation (1) can be justified from first principles. First, the two-centre character of the covalent bond energy follows from either chemical pseudopotential (Anderson 1969) or muffin-tin orbital (Andersen and Jepsen 1984) theory, where a judicious choice of localized basis enable the necessary one-electron

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secular equation to be written in a two-centre format. Secondly, the pairwise nature of the repulsive term can be justified from within the Harris–Foulkes variational scheme (Harris 1985, Foulkes 1987), which allows the density-functional ground-state energy to be (approximately) written in a one-electron eigenvalue sum plus pair potential form (Foulkes and Haydock 1989, Sutton *et al* 1988).

In practice, although providing an appealing conceptual framework to work within, the success and applicability of any tight-binding (TB) scheme critically rests on a suitable parametrization or construction of the constituent two-centre hopping integrals and pair potential. For example, Harrison's (1980) commonly used 'universal' inverse-square scaling with interatomic separation R for the hopping integrals, together with an empirical form for the pair potential (say) $\varphi \sim R^{-4}$, is only valid close to its fitted regime of fourfold coordinated semiconductors about equilibrium separations. Outside this range the description is poorer (Paxton *et al* 1987, Paxton 1989). Although alternative scalings can extend this range to include qualitatively close-packed systems and predict the favoured geometries of silicon microclusters (Goodwin *et al* 1989), in general there is no guarantee *a priori* that a semiempirical parametrization will be applicable outside its fitted domain. This *transferability* between environments must always be tested and weighed against previous benchmark results. At the other extreme, transferable, environment-independent hopping integrals constructed from some *fixed* basis functions tend to have long-range tails that bring in too many two-centre and non-negligible three-centre integrals. Up to sixth-nearest-neighbour interactions need to be included to obtain a reasonable silicon band structure if a basis of pseudo-atomic orbitals are used (Jansen and Sankey 1987). On the other hand more localized orbitals (Hoshino *et al* 1985, 1986, Anderson 1968) that give short-ranged hopping integrals suitable for molecular dynamic simulations also tend to be strongly environment-dependent. In the case of the pair potential there is a general dearth of knowledge as to appropriate functional forms to use. Only for simple metals (Pettifor and Ward 1984) using second-order pseudopotential theory and for the germanium dimer (Foulkes and Haydock 1989) using the Harris–Foulkes scheme have explicit forms been constructed. Otherwise in the literature the pair potential has always been modelled empirically by choosing some simple functional form and fitting any free parameters to benchmark *ab initio* or experimental results.

In this paper we construct, for the simplest case of single hydrogenic s orbitals, an analytic pair potential and hopping integral by working within the Harris–Foulkes scheme and using a chemical pseudopotential basis. The limitations of using a transferable TB parametrization are then studied by comparing the two separate cases where the basis orbitals are either fixed or allowed to relax to the local environment. The assumed pairwise nature of the repulsive energy is investigated by explicitly estimating the errors incurred in keeping only two-centre terms in the cluster expansion of the exchange–correlation functional. Lastly the physical decomposition of the binding energy is used to gain information on the equilibrium and asymptotic behaviour of the pair potential.

The layout of the paper is as follows. In section 2 general stationary functionals and the specific Harris–Foulkes scheme are described. Applying the latter to the hydrogen dimer, problems in constructing unique tight-binding hopping integrals and pair potentials are discussed. In sections 3 and 4 we derive a new hopping integral and pair potential by coupling the Harris–Foulkes scheme with Anderson's chemical pseudopotential theory. Modelling exchange–correlation effects within the $X\alpha$ approximation and using a variational representation of the chemical pseudopotential orbitals, explicit closed

analytic expressions for these functions are obtained. In section 5 the limitations of using fixed transferable parametrization of the hopping integral and pair potential are determined variationally, and estimates of cluster expansion errors of the exchange–correlation functional are evaluated. Finally the resulting fixed pair potential and hopping integral are plotted and the relative importance of various contributions to the cohesive energy are discussed.

2. The Harris–Foulkes scheme

2.1. Stationary functionals

Although density-functional (DF) theory has provided important benchmark *ab initio* calculations, and a formal foundation to a one-electron picture of solids (see e.g. Jones and Gunnarsson 1989), its inherent self-consistent nature makes it computationally costly. To reduce this limitation, alternative functionals have been suggested that provide approximations to the DF ground-state energy (Dunlap *et al* 1979, Harris 1985, Foulkes 1987). Exploiting the variational principle and expanding the DF energy functional about V^{in} and ρ^{in}, initial guesses for the ground-state one-electron potential and valence density respectively, a general class of these functionals (Jacobsen *et al* 1987, Foulkes and Haydock 1989) is defined by

$$E[V^{in}, \rho^{in}] = \sum_i n_i \varepsilon_i[V^{in}] - \int \rho^{in}(\tfrac{1}{2}V_H[\rho^{in}] + \mu_{xc}[\rho^{in}]) \, d\mathbf{r}$$

$$+ E_{xc}[\rho^{in}] + E_N - \int \rho^{in}(V^{in} - V_{KS}[\rho^{in}]) \, d\mathbf{r} \tag{2}$$

where

$$V_{KS}[\rho^{in}] = V_{ps}^{ion} + V_H[\rho^{in}] + \mu_{xc}[\rho^{in}] \tag{3}$$

is the Kohn–Sham one-electron potential evaluated at ρ^{in}. Here the 'inert' core electrons are incorporated within the pseudopotential V_{ps}^{ion}, and the Hartree and exchange–correlation potentials are denoted by $V_H[\rho] = \int \rho/|\mathbf{r} - \mathbf{r}'| \, d\mathbf{r}'$ and $\mu_{xc}[\rho] = \delta E_{xc}[\rho]/\delta\rho$, where $E_{xc}[\rho]$ is the usual exchange–correlation functional. E_N is the ion–ion interaction. The eigenvalues ε_i of state i making up the band term are obtained from the effective one-electron equation

$$(-\nabla^2 + V^{in})\psi_i = \varepsilon_i \psi_i. \tag{4}$$

Once this has been solved, an output charge density

$$\rho^{out} = \sum_i n_i |\psi_i|^2 \tag{5}$$

may be constructed from the eigenstates ψ_i and their occupation numbers n_i.

The strength of this approximate scheme, over a conventional solution of the Kohn–Sham DF equations (Kohn and Sham 1965), is that no self-consistent cycling is needed. Only a knowledge of V^{in} and ρ^{in} is required to estimate the DF ground-state energy E_{gs}, incurring second-order errors of the form

$$E_{gs} = E[V^{in}, \rho^{in}] + O((\rho^{out} - \rho_{gs})^2) + O((\rho^{out} - \rho^{in})^2)$$

$$+ O((\rho^{out} - \rho^{in})(V^{in} - V_{KS}[\rho^{in}])). \tag{6}$$

Although the above functional applies to any choice of V^{in} and ρ^{in}, a simpler form can be obtained by letting $V^{in} = V_{KS}[\rho^{in}]$. In this special case equation (2) reduces to the following functional, independently introduced by Harris (1985) and Foulkes (1987):

$$E_{HF}[\rho^{in}] = \sum_i n_i \varepsilon_i [V_{KS}[\rho^{in}]] - \int \rho^{in}(\tfrac{1}{2}V_H[\rho^{in}] + \mu_{xc}[\rho^{in}])\, dr$$
$$+ E_{xc}[\rho^{in}] + E_N. \tag{7}$$

As with the more general expression, the Harris–Foulkes functional is stationary, attaining the DF ground-state energy, only when the initial trial density ρ^{in} equates with the true ground-state density ρ_{gs}. Otherwise errors are second order in $\rho^{out} - \rho^{in}$ and $\rho^{out} - \rho_{gs}$, and the accuracy of the Harris–Foulkes energy depends on the choice of ρ^{in}. One form used here, which is within the spirit of tight binding, is to assume a simple superposition of atomic or pseudo-atomic densities ρ_A, namely

$$\rho^{in} = \sum_A \rho_A. \tag{8}$$

Using this form the Harris–Foulkes scheme has provided good estimates of full self-consistent DF calculations for diatomic molecules (Harris 1985, Foulkes and Haydock 1989, Averill and Painter 1990), bulk metals and semiconductors (Polatoglou and Methfessel 1988) and more recently first-row transition metals (Paxton *et al* 1990). Even for strongly ionic systems good approximations can be obtained. For example, for the compound NaCl the DF binding energy, lattice constant and bulk modulus are all estimated to within 10%, 1% and 11% respectively (Polatoglou and Methfessel 1988). For ionic molecules such as LiF the results are poorer, although (as in general) improvements are possible if a limited degree of self-consistency is incorporated and the atomic densities are allowed to relax to their environment (Averill and Painter 1990). Similarly recent work on aluminium (Finnis 1990) has also shown that if the atomic densities are renormalized to shrink the range of their tails then good estimates of surface and vacancy formation energies can be obtained.

2.2. The hydrogen dimer

As a preliminary step in constructing TB hopping integral and pair potential we calculate the density-functional (DF) and Harris–Foulkes (HF)[†] total energies for the hydrogen molecule, by following Gunnarsson and Lundqvist (1976) and using a variational 1s minimal basis,

$$\chi_{A,B}(r) = (\xi^3/\pi)^{1/2}\exp(-\xi r_{A,B}). \tag{9}$$

Here r_i ($i = A, B$) are distances from the atomic sites A and B situated a distance R apart. In order to obtain simple expressions for the exchange–correlation energy terms we approximate the local density exchange–correlation functional with the $X\alpha$ form, so that $\mu_{xc}[\rho] = \delta E_{xc}[\rho]/\delta\rho = \tfrac{4}{3}\varepsilon_{xc}(\rho)$ is proportional to $-\alpha\rho^{1/3}$ (Slater 1974). The total energy of the hydrogen molecule can then be written within the DF and HF approximations as

$$E_{DF(HF)} = [2\xi^2/(1+S)][1 - (K+S)] - [2\xi/(1+S)](2 - J - 2K)$$
$$+ 2/R + E^{ee}_{DF(HF)} + E^{xc}_{DF(HF)} \tag{10}$$

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† We hope the reader will not confuse HF as an abbreviation for either Hartree–Fock or Hellmann–Feynman.

where the common first three terms are the kinetic, electron–ion and ion–ion energies. The relevant electron–electron and exchange–correlation contributions are given by

$$E_{DF}^{ee} = [\xi/(1+S)^2](\tfrac{5}{4} + J' + 4L + 2K')$$
$$E_{HF}^{ee} = [2\xi/(1+S)](\tfrac{5}{4} + J' + 2L) - \xi(\tfrac{5}{4} + J') \tag{11}$$

and

$$E_{DF}^{xc} = E_{xc}[\rho^{out}] = -9\alpha\left(\frac{3}{64\pi}\right)^{1/3}\frac{1}{(1+S)^{4/3}}I_1^{xc}$$

$$E_{HF}^{xc} = E_{xc}[\rho^{in}] + \int (\rho^{out} - \rho^{in})\mu_{xc}[\rho^{in}] \tag{12}$$

$$= -9\alpha\left(\frac{3}{64\pi}\right)^{1/3}\left(\frac{3-S}{3(1+S)}I_2^{xc} + \frac{8}{3(1+S)}I_3^{xc}\right).$$

Here the overlap integral between the basis functions is denoted by $S = \langle \chi_A | \chi_B \rangle$ and the input and output densities are given by

$$\rho^{in} = \rho_A + \rho_B$$
$$\rho^{out} = 2|\psi_{gs}|^2 = [1/(1+S)](\rho_A + \rho_B + 2\chi_A\chi_B) \tag{13}$$

where $\rho_i(r) = |\chi_i|^2$ $(i = A, B)$ are atomic densities and the bonding orbital wavefunction is

$$\psi_{gs} = \{1/[2(1+S)]^{1/2}\}(\chi_A + \chi_B). \tag{14}$$

The integrals K, K', J, J', S and L are listed by Slater (1963). All have closed analytic forms except for the second-order exchange integral K', which we interpolate using an accurate rational polynomial approximation (Abramowitz and Stegun 1965) for the related exponential integral. In the appendix we give the exchange–correlation integrals I_1^{xc}, I_2^{xc} and I_3^{xc}, and show how by changing to spheroidal coordinates these may be reduced to a few one-dimensional integrals that can be evaluated using standard numerical integration routines. In passing, obvious typographical errors in Slater's (1963) table 3-1 for the energy integrals K' and $\int \chi_A(-\nabla^2)\chi_B \, dv$ were corrected.

In figure 1 the DF and HF minimal basis energies are displayed (equation (10)). For the DF benchmark case, an optimal exponent $\xi_{DF}(R)$ was determined that minimized the energy for each fixed interatomic separation R, with the *exchange–correlation measure* α chosen to ensure that Kolos and Wolniewicz's (1965) accurate equilibrium binding energy is reproduced at equilibrium. The HF energy curve was then plotted for this fixed value $\alpha = 0.8266$ and for the same optimal DF exponent (i.e. $\xi_{HF}(R) \equiv \xi_{DF}(R)$). With this latter constraint, differences between our minimal basis solutions are only in the exchange–correlation and electron–electron terms (equations (11) and (12)).

The HF scheme thus provides an excellent approximation to the full 'self-consistent', minimal basis DF solution, being indistinguishable from it in figure 1. In agreement with recent work of Averill and Painter (1990) the success of this scheme can be attributed
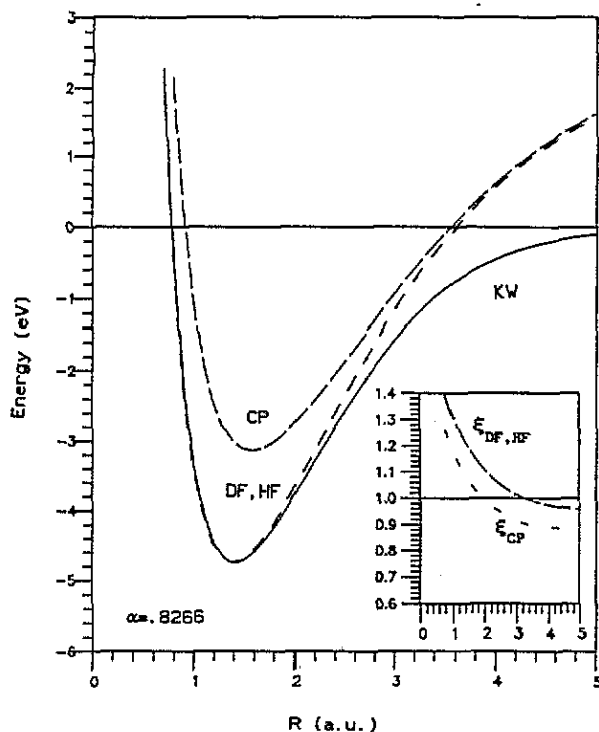
Figure 1. Comparison of the minimal basis density-functional (DF), Harris–Foulkes (HF) and chemical pseudopotential (CP) binding energies for diatomic hydrogen. The inset gives the optimal orbital exponents $\xi_{DF}(R)$ and $\xi_{CP}(R)$ that minimize the DF and CP binding energies. For the HF exponent we set $\xi_{HF}(R) = \xi_{DF}(R)$. In all cases $\alpha = 0.8266$. The full curve gives the accurate results of Kolos and Wolniewicz (1965) (KW).

to the cancellation of (positive) electron–electron and (negative) exchange–correlation correction terms, namely

$$\Delta E^{ee} = E^{ee}_{DF} - E^{ee}_{HF} = \frac{1}{2} \int \frac{\Delta \rho \, \Delta \rho'}{|r - r'|} = \frac{\xi}{(1 + S)^2} [2K' - 4SL + S^2(\tfrac{5}{4} + J')] \tag{15}$$

and

$$\Delta E^{xc} = E^{xc}_{DF} - E^{xc}_{HF} = \frac{1}{2} \int \Delta \rho \, \Delta \rho' \left(\frac{\delta^2 E_{xc}}{\delta \rho^2} \right)_{\rho = \rho^{in}} + O((\Delta \rho)^3) \tag{16}$$

where $\Delta \rho = \rho^{out}(r) - \rho^{in}(r)$ and $\Delta \rho' = \rho^{out}(r') - \rho^{in}(r')$. From their test studies of diatomic molecules Averill and Painter (1990) found this cancellation $(-\Delta E^{xc}/\Delta E^{ee})$ to range from 0.79 for weakly bonded molecules such as Be_2 to 0.13 for strongly bonded ionic molecules such as LiF. In figure 2 for our minimal basis treatment of diatomic hydrogen, owing to the same exponent being used for both the DF and HF cases, we find this cancellation is almost complete. Further, figure 2 also emphasizes the purely stationary nature of the HF scheme, in that it is not guaranteed to be a variational upper bound of the DF energy. For $R \geqslant 1.6$ au, it is in fact lower in energy.

The appropriateness of using a simple minmal basis treatment and modelling exchange–correlation effects within the $X\alpha$ approximation is also borne out, with the restricted DF solution reproducing well the accurate results of Kolos and Wolniewicz (1965) for equilibrium separations. For large R there are well known discrepancies due to the incomplete cancellation of the exchange–correlation functional $E_{xc}[\rho]$ with the electron–electron term, when the exact functional form of the former is unknown (Harris
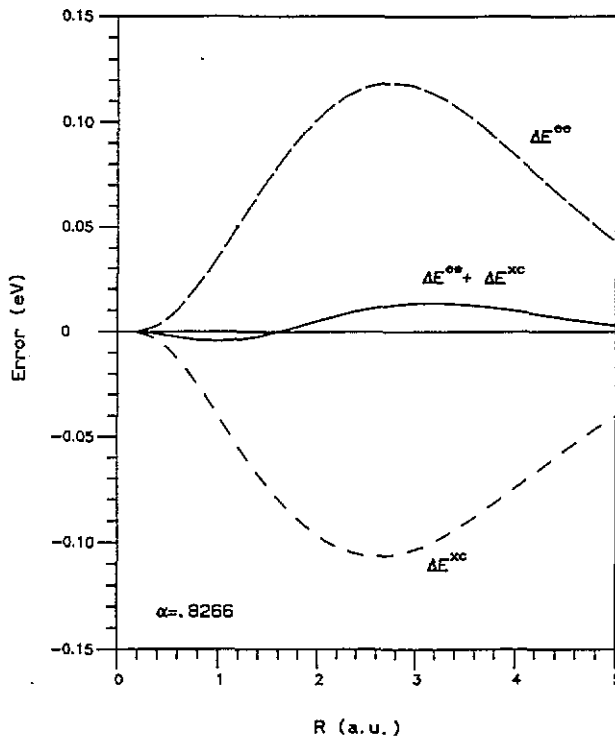
Figure 2. Cancellation of the exchange–correlation and electron–electron correction terms $\Delta E^{\text{ce(xc)}} = E^{\text{ce(xc)}}_{\text{DF}} - E^{\text{ce(xc)}}_{\text{HF}}$. The full curve gives the total energy difference $\Delta E = E_{\text{DF}} - E_{\text{HF}} = \Delta E^{\text{ce}} + \Delta E^{\text{xc}}$ between the density-functional (DF) and Harris–Foulkes (HF) binding energy curves of figure 1.

1984). This problem may be removed by allowing a spin-density state to evolve for $R \geqslant 3.2$ au (Gunnarsson and Lundqvist 1976).

Although the HF scheme gives a simpler expression than the DF minimal basis treatment, in that all terms are analytic (besides the exchange–correlation integrals), it still does not enable the total energy to be written generally in the TBB form of equation (1). Primarily, this is due to factors like $1/(1 + S)$, which are not well approximated by the first few terms in a binomial expansion, as at equilibrium $S \sim 0.7$. This prevents us from constructing a separable pairwise non-orthogonality contribution. To overcome this problem we turn to chemical pseudopotential theory.

3. Chemical pseudopotentials

3.1. General theory

Within any minimal basis solution of the one-electron equation (4), there exists an extra degree of freedom that can be exploited, namely the choice of basis functions. One possible set is given by Anderson's (1968, 1969, 1984) chemical pseudopotential (CP) equation. In order to define the localized orbital $|A\rangle$, the one-electron potential

$$V^{\text{in}} = V_A + \sum_{B \neq A} V'_B \tag{17}$$

is split into the potentials V_A and V'_B associated with site A and its neighbouring sites B

respectively. Each CP orbital $|A\rangle$ is then determined by solving the non-linear eigenvalue equation

$$\left(-\nabla^2 + V_A + \sum_{B \neq A} \hat{V}'_B\right)|A\rangle = E_A|A\rangle \tag{18}$$

where the effects of neighbouring sites are felt through the screened pseudopotentials

$$\hat{V}'_B = (1 - |B\rangle\langle B|)V'_B. \tag{19}$$

Expanding the one-electron eigenfunctions $|\psi_i\rangle$ in terms of these basis orbitals $\{|A\rangle\}$ results in a secular eigenvalue equation that is exactly two-centre in form, namely

$$\det|\langle B|V'_B|A\rangle(1 - \delta_{AB}) - (\varepsilon_i - E_A)\delta_{AB}| = 0. \tag{20}$$

The non-orthogonality matrix elements $S_{AB} = \langle A|B\rangle$ enter linearly as a repulsive shift to the CP eigenvalues,

$$E_A = \langle A|-\nabla^2 + V_A|A\rangle + \sum_{B \neq A} \langle A|V'_B|A\rangle - \sum_{B \neq A} S_{AB}\langle B|V'_B|A\rangle. \tag{21}$$

The price of absorbing all 'three-centreness' into the definition of the CP orbitals is twofold. First, these basis orbitals are environment-dependent and have to be determined self-consistently (see Anderson 1968, Hoshino *et al* 1985, 1986). Secondly, the secular equation (20) in general is non-Hermitian. For a comprehensive account of these subtleties and how CP orbitals are used in practice, consult either Bullett's (1980) review article or Anderson's (1984) paper.

3.2. Application within the Harris–Foulkes scheme

It is clear from equation (17) that there is no unique way to separate the input potential into V_A and V'_B. However, in order to preserve the explicit two-centre form of the secular equation (20) and write the HF energy functional within a TBB framework, V_A and V'_B must be constrained to be two-centre in nature. To do this for the HF one-electron potential $V_{KS}[\rho^{in}]$ where $\rho^{in} = \Sigma \rho_A$, we expand the many-body exchange–correlation potential about the site A as

$$\mu_{xc}[\rho^{in}] = \mu_{xc}[\rho_A] + \sum_{B \neq A} (\mu_{xc}[\rho_A + \rho_B] - \mu_{xc}[\rho_A]) + \cdots. \tag{22}$$

Neglecting three- and higher many-centre terms results in the following (asymmetric) decomposition:

$$V_A = (-2/r_A) + \int \rho_A/|r - r'| + \mu_{xc}(\rho_A)$$

$$V'_B = (-2/r_B) + \int \rho_B/|r - r'| + \mu_{xc}(\rho_A + \rho_B) - \mu_{xc}(\rho_A). \tag{23}$$

For the dimer this is exact, $V_{KS}[\rho^{in}] = V^{in} = V_A + V'_B$. Otherwise, it is only approximate, $V_{KS}[\rho^{in}] \neq V^{in} = V_A + \Sigma_{B \neq A} V'_B$.

Although the choice of ρ_A may be independent of basis orbitals $\{|A\rangle\}$, for simplicity we take it to be of the form $\rho_A = |\langle r|A\rangle|^2$. In this case all explicit pairwise contributions to the HF energy stemming from the potential $\mu_{xc}(\rho)$ cancel. Discarding three- and higher

many-centre terms, the only remaining exchange–correlation terms originate from the functional

$$E_{xc}[\rho^{in}] = \int \rho^{in} \varepsilon_{xc}(\rho^{in}). \tag{24}$$

To ensure that these are pairwise we follow Foulkes and Haydock (1989) and keep only two-centre terms in the many-body cluster expansion,

$$E_{xc}[\rho^{in}] = \sum_A E_{xc}[\rho_A] + \frac{1}{2} \sum_A \sum_{B \neq A} (E_{xc}[\rho_A + \rho_B] - E_{xc}[\rho_A] - E_{xc}[\rho_B]) + \dots. \tag{25}$$

If all sites are equivalent, contributions such as

$$U_{xc} = E_{xc}[\rho^{in}] - \sum_A E_{xc}[\rho_A] \equiv \sum_A \int \rho_A [\varepsilon_{xc}(\rho^{in}) - \varepsilon_{xc}(\rho_A)] \tag{26}$$

are approximated by

$$\bar{U}_{xc} = \frac{1}{2} \sum_A \sum_{B \neq A} (E_{xc}[\rho_A + \rho_B] - E_{xc}[\rho_A] - E_{xc}[\rho_B])$$

$$\equiv \sum_A \int \rho_A \sum_{B \neq A} [\varepsilon_{xc}(\rho_A + \rho_B) - \varepsilon_{xc}(\rho_A)]. \tag{27}$$

Comparing the second lines of equations (26) and (27), the cluster expansion (25) is consistent with using the expansion (22) about site A for the exchange–correlation energy density $\varepsilon_{xc}(\rho)$.

Working through the generalized HF functional (equation (2)), using the specific CP basis to include linearly non-orthogonality effects and keeping only pairwise contributions in both the cluster and the on-site expansions of the exchange–correlation terms, the ground-state energy for hydrogen can be cast in the following TBB form:

$$E[V^{in}, \rho^{in}] \cong \sum_{i,occ} (\varepsilon_i - \varepsilon_0) + \frac{1}{2} \sum_A \sum_{B \neq A} (\varphi_{es} + \varphi_{no} + \varphi_{xc}) + \sum_A E_{at}. \tag{28}$$

The attractive bond energy comes from summing over the occupied eigenvalues ε_i with reference to the energy level $\varepsilon_0 = E_A$. The ε_i are determined by solving the secular equation (20), where the related hopping integral is given by

$$ss\sigma = \langle B | V'_B | A \rangle. \tag{29}$$

The pair potential φ is defined by grouping together the following non-orthogonality, exchange–correlation and classical electrostatic terms:

$$\varphi_{no} = -2S_{AB}\langle B | V'_B | A \rangle$$

$$\varphi_{xc} = 2 \int \rho_A(\varepsilon_{xc}[\rho_A + \rho_B] - \varepsilon_{xc}[\rho_A]) \tag{30}$$

$$\varphi_{es} = \int \rho_A(-2/r_B) + \int \rho_B(-2/r_A) + \int \rho_A\rho_B/|r - r'| + 2/R.$$

The last term in equation (28),

$$E_{at} = \langle A | -\nabla^2 | A \rangle + \int \rho_A(-2/r_A) + \tfrac{1}{2} \int \rho_A\rho_A/|r - r'| + E_{xc}[\rho_A] \tag{31}$$

is the energy of a free neutral atom (as calculated within DF theory) and gives the reference energy.

To evaluate the right-hand side of (28) it is necessary to determine or estimate the environment-dependent CP orbitals $\{|A\rangle\}$ defined by the non-linear equation (18). This is a hard self-consistency problem, which has only been tackled in the simplest cases (Anderson 1969, Hoshino *et al* 1985). Instead, we choose a variational solution and represent each CP basis function with a simple 1s Slater orbital, $\langle r|A\rangle \simeq (\xi^3/\pi)^{1/2} \exp(-\xi r_A)$. The hopping integral, pair potential components and reference energy given by equations (29), (30) and (31) then reduce to the following expressions:

$$\text{ss}\sigma = \xi(K + L) - 9\alpha[3/(64\pi)]^{1/3}(I_3^{xc} - I_4^{xc})$$
$$\varphi_{no} = -2S(\text{ss}\sigma)$$
$$\varphi_{xc} = -9\alpha[3/(64\pi)]^{1/3}I_2^{xc} - 2(-\xi\alpha^*/16)$$
$$\varphi_{es} = \xi(2J + J') + 2/R \tag{32}$$
$$E_{at} = \xi^2 - 2\xi + 5\xi/8 - \xi\alpha^*/16$$

where $\alpha^* = \alpha(243/4)[3/(64\pi^2)]^{1/3}$ and the exchange–correlation integral I_3^{xc} is defined in the appendix. As before, the integrals K, L, J, J' and S are given by Slater (1963).

In figure 1 the resulting CP ground-state energy for diatomic hydrogen is plotted. In this case, equality holds in equation (28) if true CP orbitals were used. The difference therefore between this and the HF solution gives some measure of the error incurred in our representation. Although large in places, this error is of a similar order to that found by Hoshino *et al* (1985), who investigated numerous minimal atomic basis representations of general localized orbitals. For H_2^+ they found that a single atomic orbital representation of Anderson's CP orbitals produced errors at equilibrium of 1.248 eV, 7.6% of the total energy, but 30% of the binding energy. Enlarging the basis set either on the single site or by extending it over neighbouring sites systematically reduces this error (Hoshino *et al* 1985, 1986). In this paper we will partially compensate for this error by adjusting the exchange–correlation parameter α, and letting $\alpha = 0.871$ (see section 5 for details).

4. Exchange–correlation integrals

Although all the necessary exchange–correlation terms in the energy expression (equation (32)) can be reduced to a few one-dimensional integrals that can be evaluated numerically (see appendix), in order to obtain explicit analytic expressions we introduce one further approximation, namely

$$(\rho_A + \rho_B)^{1/3} \simeq \begin{cases} \rho_A^{1/3}[1 + \frac{1}{3}(\rho_B/\rho_A)] & r_A < r_B \\ \rho_B^{1/3}[1 + \frac{1}{3}(\rho_A/\rho_B)] & r_A > r_B. \end{cases} \tag{33}$$

Changing to spheroidal coordinates (see appendix) then enables all exchange–correlation integrals to be estimated to better than 6%. For the range of interest, $R \geqslant 1$, this error is less than 2%. The resulting hopping integral and pair potential have the following analytic forms:

$$\text{ss}\sigma(\xi, R, \alpha)/\xi \simeq e^{-w}(5/8w - 7/4) + e^{-3w}(-1/4 - 5/8w)$$
$$+ \alpha(243/2)[3/(64\pi^2)]^{1/3}[e^{-w}(15/16w - 5/12)$$
$$+ e^{-4w/3}(14w/135 + 7/45 - 939/500w) + e^{-5w/3}(15/16w + 1/4)$$
$$+ (1/15) e^{-3w}(9/200w + 1/30)] \tag{34}$$

$$\varphi(\xi, R, \alpha)/2\xi \simeq e^{-2w}(5/8 + 1/w - 3w/4 - w^2/6) - S(w)[ss\sigma(\xi, R, \alpha)/\xi]$$
$$+ \alpha(243/64)[3/(64\pi^2)]^{1/3}[e^{-4w/3}(189/64w - 11/12 - 11w/18)$$
$$- e^{-2w}(4/3 + 3/w) + e^{-4w}(1/24 + 3/64w)]. \tag{35}$$

Here the orbital overlap is given by $S(w) = (1 + w + \frac{1}{3}w^2)\exp(-w)$ where $w = \xi R$ and the units of energy are rydbergs.

5. Transferability and the pair potential

5.1. A first-nearest-neighbour model

To study the limitations of using an environment-independent TB parametrization we focus our attention on a first-nearest-neighbour model consisting of N equivalent sites. The tight-binding energy (28) per atom can then be written as

$$E/N = \varepsilon = \tfrac{1}{2}Z[ss\sigma(\xi, R, \alpha)\Theta + \varphi(\xi, R, \alpha)] + C. \tag{36}$$

Here Θ is the bond order between s orbitals on neighbouring sites, Z is the local coordination and with reference to the exact free atomic energies the constant C is given by

$$C = \xi^2 - 2\xi + 5\xi/8 - \xi\alpha^*/16 - (-1). \tag{37}$$

As hydrogen atoms are brought together, the Slater 1s orbitals may be allowed to relax to the local environment by optimizing the exponent ξ so that the energy expression (36) is minimized at each interatomic separation R. For fixed α, by exploiting the functional form of the hopping integral $ss\sigma(R, \xi, \alpha) = \xi F(w)$ and pair potential $\varphi(R, \xi, \alpha) = \xi G(w)$ (equations (34) and (35)) and denoting differentiation by a prime, this variationally optimal exponent has the parametrized form

$$\xi(w) = \xi_\infty - \tfrac{1}{4}Z[(F\Theta + G) + w(F'\Theta + G')]$$
$$R(w) = w/\xi(w). \tag{38}$$

At infinite separation it has the value $\xi_\infty = \frac{1}{2}(\alpha^*/16 + 11/8)$, which is only equal to 1 (the hydrogenic free-atom limit) if $\alpha = 0.9793$, the value needed to give complete cancellation of the self electron–electron term. For equilibrium separations $R_{eq} = w_{eq}/\xi_{eq}$ the optimal exponent (38) and binding energy (36) simplify further to give

$$\xi_{eq} = \xi(w_{eq}) = \xi_\infty - \tfrac{1}{4}Z[F(w_{eq})\Theta + G(w_{eq})]$$

and

$$E_{eq}/N = \varepsilon_{eq} = \varepsilon(\xi_{eq}, R_{eq}) = 1 - (\xi_{eq})^2. \tag{39}$$

To relate the above optimal case when the orbital exponent is environment-dependent and depends on the interatomic separation R to the transferable case where the exponent ξ is fixed we exploit the identities

$$(\partial E/\partial \xi)_{\xi_{eq}, R_{eq}} = (\partial E/\partial R)_{\xi_{eq}, R_{eq}} = 0$$
$$w_{eq} = \xi_{eq} R_{eq} = \xi R_{eq}(\xi). \tag{40}$$

The equilibrium binding energy $E_{eq}(\xi)$, atomic separation $R_{eq}(\xi)$ and bulk modulus
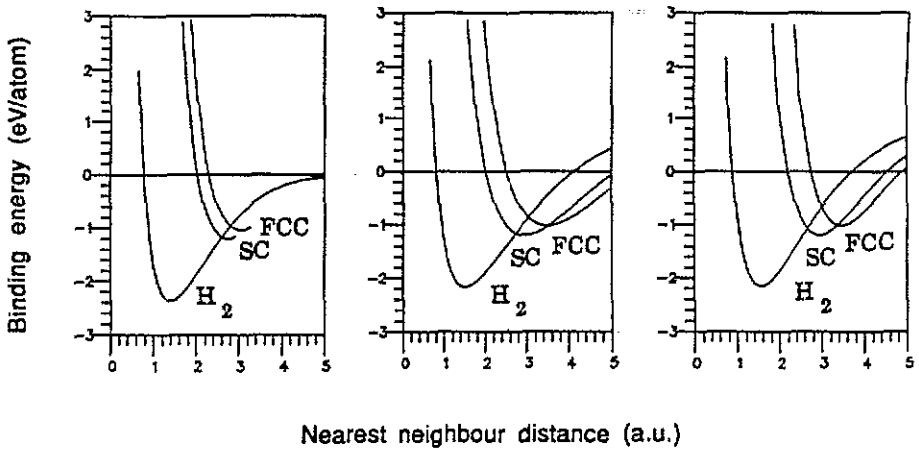
Figure 3. Binding energies for diatomic (H_2) and bulk metallic simple cubic (SC) and face centred cubic (FCC) hydrogen. Results obtained within a first-nearest-neighbour TBB model, using the analytic pair potential and hopping integral of equations (34) and (35), are compared for cases in which the orbital exponent is either environment-dependent (central panel) or fixed at the value $\xi = 1.043$ (right panel). In both cases $\alpha = 0.871$. Benchmark calculations of Kolos and Wolniewicz (1965) and Min *et al* (1984) (left panel) are plotted for reference.

$B_{eq}(\xi)$ corresponding to the fixed exponent ξ can then be expanded about the optimal equilibrium exponent ξ_{eq} and separation $R_{eq} = R_{eq}(\xi_{eq})$ to give

$$E_{eq}(\xi) = E_{eq} + O((\Delta\xi)^2, (\Delta R)^2, \Delta\xi\Delta R)$$

$$R_{eq}(\xi) = w_{eq}/\xi = R_{eq}(1 - \Delta\xi/\xi_{eq} + \ldots) \tag{41}$$

$$B_{eq}(\xi) = B_{eq}\tau_{eq}(\xi/\xi_{eq})^4 = B_{eq}\tau_{eq}(1 + 4\Delta\xi/\xi_{eq} + \ldots).$$

Here B_{eq} and E_{eq} are the optimal equilibrium bulk modulus and binding energy, and

$$\tau_{eq} = 1 + \tfrac{1}{2}(R_{eq}/\xi_{eq})^2(\partial^2 E/\partial R^2)_{\xi_{eq}, R_{eq}}. \tag{42}$$

Differences between using a fixed or optimal exponent are second order in $\Delta\xi = \xi - \xi_{eq}$ for the binding energy (as $\Delta R = R(\xi) - R_{eq} \sim \Delta\xi$) and first order in $\Delta\xi$ for the equilibrium separation, whereas an extra enhancement factor τ_{eq} augments B_{eq} for the bulk modulus $B_{eq}(\xi)$.

In figure 3 we display the binding energy curves for diatomic and bulk metallic simple cubic (SC) and face centred cubic (FCC) hydrogen. The leftmost panel gives the accurate calculations of Kolos and Wolniewicz (1965) and Min *et al* (1984), with which we compare our first-nearest-neighbour TB results obtained using the derived analytic pair potential and hopping integral of equations (34) and (35). The central panel gives the energy curves obtained when the optimal exponents defined by equation (38) and plotted in figure 4 are used. For the rightmost panel the exponent ξ is fixed to its equilibrium value (39) for the optimal simple cubic curve, namely $\xi = 1.043$ (see table 1). In both the latter TB cases the exchange–correlation parameter α is chosen to reproduce the accurate equilibrium binding energy of Min *et al* (1984) for the bulk simple cubic case, namely $\alpha = 0.871$.
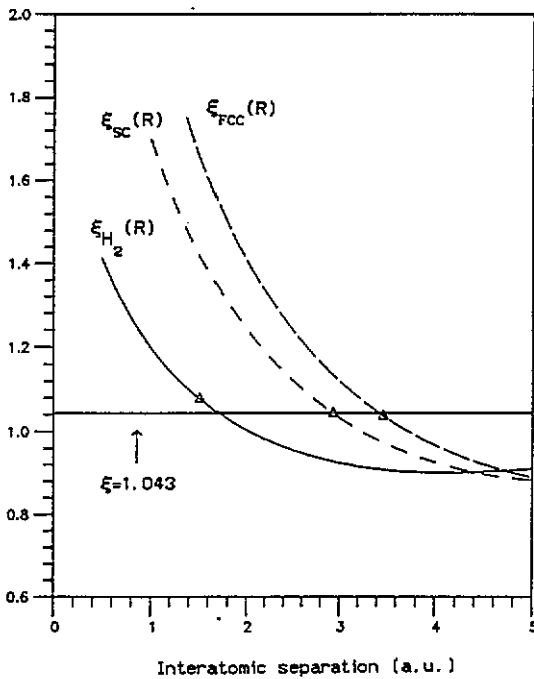
Figure 4. Comparison of the optimal orbital exponents defined by equation (40) for diatomic (H_2) and bulk metallic simple cubic (SC) and face centred cubic (FCC) hydrogen. Equilibrium values are denoted by open triangles. In all cases $\alpha = 0.871$. For reference the fixed exponent $\xi = 1.043$ is also plotted.

Table 1. Equilibrium values of optimal orbital exponents, $\xi_{eq} = \xi(R_{eq})$, for $\alpha = 0.871$.

Structure	ξ_{eq}
FCC	1.0368
SC	1.0430
H_2	1.0767

Although both the TB cases qualitatively reproduce the benchmark equilibrium separations and binding energies (see table 2), as expected from our previous analysis (equation (41)) the dominant difference between the environment-dependent and environment-independent TB cases are in the equilibrium curvatures. Taking the FCC lattice as an example, $\Delta\xi \sim 0.006$ is small, so the percentage errors incurred in the equilibrium binding energy and atomic separation in using the exponent $\xi = 1.043$ instead of the optimal exponent $\xi_{FCC}(R)$ are only 0.1% and 0.6%. For the bulk modulus, owing to the extra enhancement factor τ_{eq} (equation (42)), the corresponding difference is 112%. Similar results are obtained for diatomic and bulk FCC hydrogen, as may be seen in table 2. This can be understood from figure 4, as although $\xi = 1.043$ is close to all the equilibrium values of the optimal exponents, denoted there by open triangles (for numerical values, see table 1), the orbital exponents are intrinsically very environment dependent. This dependence can be dramatically demonstrated by taking the orbital exponent to be a fixed function of the interatomic separation, say $\xi = \xi_{sc}(R)$. In this case the hydrogen dimer is incorrectly predicted to be less stable in energy than bulk SC hydrogen!

Table 2. Equilibrium binding energies E_0, interatomic separations R_0, bulk moduli B_0 and vibrational frequencies v_0 for the metallic and diatomic hydrogen curves given in figure 3, $\alpha = 0.871$.

FCC	Min *et al* (1984)	$\xi = \xi_{FCC}(R)$	$\xi = 1.043$
E_0 (eV/atom)	−1.038	−1.019	−1.018
R_0 (au)	3.045	3.468	3.447
B_0 (Mbar)	1.251	0.614	1.299

SC	Min *et al* (1984)	$\xi = \xi_{SC}(R)$	$\xi = 1.043$
E_0 (eV/atom)	−1.195	−1.195	−1.195
R_0 (au)	2.752	2.935	2.935
B_0 (Mbar)	1.123	0.615	1.093

H$_2$	Kolos and Wolniewicz (1965)	$\xi = \xi_{H_2}(R)$	$\xi = 1.043$
E_0 (eV/atom)	−2.374	−2.169	−2.152
R_0 (au)	1.401	1.511	1.560
v_0 (cm^{-1})	4380	3699	4092

From this analytic first-nearest-neighbour study of hydrogen it is not possible to reproduce globally 'stiffness' properties that depend on the equilibrium curvatures using a fixed, environment-independent TB parametrization. This agrees with Goodwin *et al*'s (1989) improved TB parametrization of silicon, which qualitatively reproduced equilibrium separation and binding energies, but only at the expense of a poorer overall fit of the equilibrium curvatures for the lattices considered.

5.2. Errors in the cluster expansion

Besides the environment dependence of the CP orbitals, the second element that governs the transferability of sso and φ is the validity of neglecting three- and higher many-centre terms in the cluster expansion for the exchange–correlation functional $E_{xc}[\rho]$ (equation (25)).

To obtain a 'back of an envelope' estimate for the errors incurred, we first consider the case of overlapping, uniform cubic electron densities,

$$\rho_A(r) = \begin{cases} 1/(8a^3) & |x - x_A|, |y - y_A|, |z - z_A| < a \\ 0 & \text{otherwise} \end{cases} \tag{43}$$

situated at positions $r_A = (x_A, y_A, z_A)$ on an infinite simple cubic lattice of interatomic separation a. Noting that there is zero overlap of ρ_A with similar densities situated at fourth- or higher nearest-neighbour separations, this system is equivalent to looking at

a free-electron gas of uniform density $\rho = a^{-3}$. Working within the $X\alpha$ approximation and letting $\varepsilon_{xc}(\rho) = -\rho^{1/3}$, U_{xc} and $\bar{U}_{xc}$ (equations (26) and (27)) can be evaluated as

$$U_{xc} = -N[1/a - 1/(2a)] = -0.5(N/a)$$
$$\bar{U}_{xc} = -N[7(2^{1/3} - 1)/(2a)] = -0.91(N/a). \tag{44}$$

This suggests that the relative errors in keeping only pairwise terms in the cluster expansion will be large, being 82% for the above system of cubic densities.

To quantify these errors explicitly for the derived pair potential of section 3.2, we recalculate U_{xc} and $\bar{U}_{xc}$ for exponential densities $\rho_A = (\xi^3/\pi) \exp(-2\xi r_A)$ in the case of the fixed TB parametrization $\xi = 1.043$ and $\alpha = 0.871$. Placing these densities on a simple cubic (SC) lattice at the equilibrium separation $R_{eq}^{SC} = 2.935$ results in a relative error of 52%. In absolute terms this is 0.25 eV/atom or 21% of the relevant *ab initio* binding energy. Similar results are obtained for the face centred cubic (FCC) lattice, where at the equilibrium separation $R_{eq}^{FCC} = 3.447$ absolute errors are obtained of 0.27 eV/atom or 26% of the *ab initio* binding energy.

These errors may be interpreted as the cost of either constraining the bulk pair potential φ to have the same functional form as that for the dimer or of keeping only pairwise terms in a many-body expansion of the repulsive energy E_{rep}. Although sizable, for the bulk systems considered these errors are of a similar magnitude. A cancellation of errors could be expected for bulk calculations where relative and not absolute energies are important.

5.3. The nature of the pair potential and hopping integral

In figure 5 we plot the resulting hopping integral and pair potential for the fixed TB parametrization $\alpha = 0.871$ and $\xi = 1.043$. To compare these derived functional forms with others used in the literature we determine their effective inverse scaling with interatomic separation R. This can be obtained for the pair potential φ by matching its logarithmic derivative

$$\mathcal{L}[\varphi(R)] = -\frac{d}{dR} \ln[\varphi(R)] \equiv -\frac{\varphi'(R)}{\varphi(R)} \tag{45}$$

with that obtained assuming an inverse power scaling, namely $\mathcal{L}[R^{-m}] = m/R$. For the particular functional form $\varphi = \xi G(w)$ (equation (35)) it scales as $\varphi \sim R^{-m}$, where $m = \mathcal{L}[\varphi]R = -wG'/G$. Similarly the hopping integral $ss\sigma = \xi F(w)$ (equation (34)) has an effective inverse scaling of $ss\sigma \sim R^{-n}$, where $n = \mathcal{L}[ss\sigma]R = -wF'/F$. In table 3, m and n are listed together with the exponent $\varkappa = m/n$, which describes the effective scaling of φ with $ss\sigma$ (i.e. $\varphi \sim ss\sigma^\varkappa$). As with Goodwin *et al*'s (1989) improved empirical scaling for silicon, where $\varkappa = 2.27$, for the equilibrium separations considered in table 3, $\varkappa$ lies in the range $2 < \varkappa < 2.5$ commonly assumed in empirical TB parametrization of sp-bonded systems (Harrison 1983, Majewski and Vogl 1987). In particular, it is interesting to note for the hydrogen dimer at $R_{eq}(\xi)$ that the value of the effective inverse power scaling exponent for the hopping integral is close to the canonical scaling of $ss\sigma \sim R^{-1}$ (Andersen and Jepsen 1984).

To discuss the equilibrium and long-range nature of the pair potential φ, in figure 6 we plot the physical decomposition of the HF energy for the hydrogen dimer as defined by equation (28). At equilibrium separations it is thus the interplay between the covalent bonding ($2ss\sigma$), non-orthogonality (φ_{no}) and exchange-correlation (φ_{xc}) terms that is
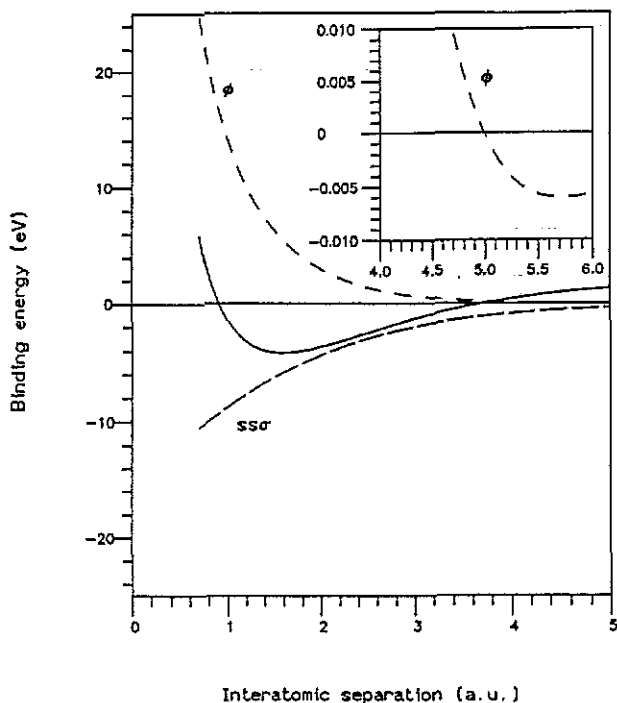
Figure 5. The resulting tight-binding hopping integral sso and pair potential φ (equations (34) and (35)) for the fixed TB parametrization $\alpha = 0.871$ and $\xi = 1.043$. For reference the binding energy of diatomic hydrogen (full curve) is also given.

Table 3. Effective scaling exponents n, m and $n = m/n$ evaluated at the face centred cubic (FCC), simple cubic (SC) and diatomic (H_2) equilibrium separations $R_{eq}(\xi)$ for the fixed TB parametrization $\alpha = 0.871$ and $\xi = 1.043$.

Structure	$R_{eq}(\xi)$	n	m	$n = m/n$
FCC	3.447	2.894	6.719	2.322
SC	2.935	2.393	5.085	2.125
H_2	1.560	1.135	2.380	2.097

important, not the classical electrostatic (φ_{es}) term, which is small in comparison. In particular, the pair potential φ is dominated by the repulsive non-orthogonality contribution φ_{no} as assumed by Harrison (1983) and Majewski and Vogl (1987). For large separations the exchange–correlation contribution (φ_{xc}) plays a more important role; for $R > 5.0$ the pair potential is attractive.

6. Conclusions

For the simplest case of a hydrogenic system we have derived from first principles an analytic pair potential and hopping integral. By exploiting their explicit functional form
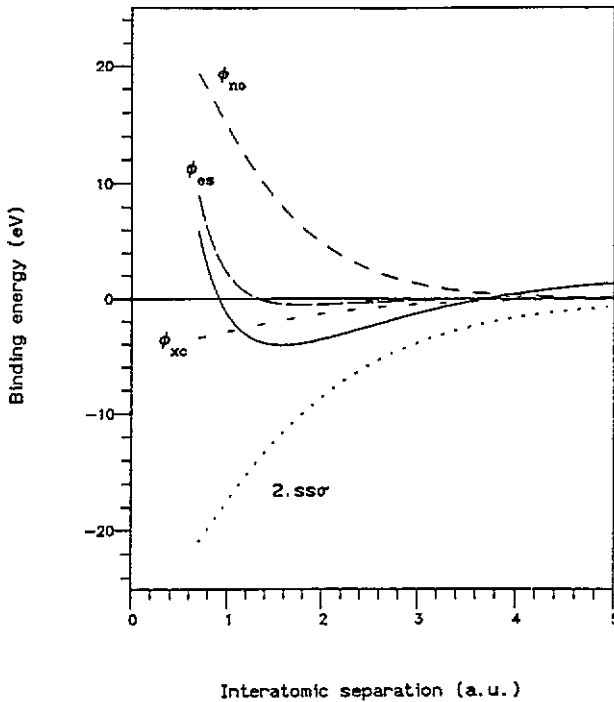
Figure 6. Breakdown of the binding energy (full curve) of diatomic hydrogen in figure 5 into terms of an electrostatic (φ_{es}), exchange–correlation (φ_{xc}), non-orthogonality (φ_{no}) and bonding ($2ss\sigma$) nature.

the cost of using a fixed, environment-independent, semiempirical parametrization was determined. It was shown that, although fully variational equilibrium binding energies and atomic separations were reproduced, it was not possible to obtain the correct equilibrium curvatures of structure types with very different local coordination using a single set of transferable parameters. This reflected the strong environment dependence of the hopping integral and pair potential. Errors incurred in keeping only pairwise terms in a cluster expansion for the exchange and correlation functional were also evaluated and shown to be large, although of a similar magnitude for the lattices considered.

Acknowledgments

Appendix

Using the notation of equation (9), the required exchange–correlation integrals used in this paper are given by

$$I_1^{xc} = \int (\chi_A + \chi_B)^{8/3} \, dv$$

$$I_2^{xc} = \int (\chi_A^2 + \chi_B^2)^{4/3} \, dv$$

$$I_3^{xc} = \int \chi_B (\chi_A^2 + \chi_B^2)^{1/3} \chi_A \, dv \tag{A1}$$

$$I_4^{xc} = \int \chi_B (\chi_A^2)^{1/3} \chi_A \, dv.$$

Besides I_4^{xc}, these integrals do not have closed analytic forms, but can be reduced to a few one-dimensional integrals by changing to spheroidal coordinates (λ, μ, β). In this system, β is the azimuthal angle about the axis joining the centres A and B, whereas the surfaces of revolution of constant λ and μ defined by

$$r_A + r_B = \lambda R$$
$$r_A - r_B = \mu R \tag{A2}$$

amount to families of ellipsoids and hyperboloids with foci at A and B. The corresponding volume element in these coordinates is

$$dv = \tfrac{1}{8} R^3 (\lambda^2 - \mu^2) \, d\lambda \, d\mu \, d\beta. \tag{A3}$$

Here we demonstrate this reduction explicitly for the integral I_2^{xc}. Substituting the expression for χ_A and χ_B (equation (9)) and changing to spheroidal coordinates results in the following triple integral for I_2^{xc}:

$$I_2^{xc} = \left(\frac{\xi^3}{\pi}\right)^{4/3} \int_1^\infty d\lambda \int_{-1}^1 d\mu \int_0^{2\pi} d\beta \frac{R^3}{8} (\lambda^2 - \mu^2) \left[\exp\left(\frac{-4\xi R\lambda}{3}\right) 2^{4/3} \cosh^{4/3}(\xi\mu R) \right]. \tag{A4}$$

Integrating over the azimuthal angle β and exploiting the identity

$$\int_x^\infty y^n \exp(-ay) \, dy \equiv \frac{\exp(-ax) n!}{a^{n+1}} \left(1 + ax + \frac{(ax)^2}{2!} + \ldots + \frac{(ax)^n}{n!} \right) \tag{A5}$$

to perform the λ integration reduces I_2^{xc} to the final one-dimensional form:

$$I_2^{xc} = \xi \left(\frac{2}{\pi}\right)^{4/3} \frac{3\pi}{8} \frac{e^{-4w/3}}{w} \left((\tfrac{9}{8} + \tfrac{3}{2}w + w^2) \int_0^w \cosh^{4/3} z \, dz - \int_0^w z^2 \cosh^{4/3} z \, dz \right). \tag{A6}$$

Similarly

$$I_1^{xc} = \frac{\xi 2^{8/3} 3}{\pi^{1/3}} \frac{e^{-4w/3}}{w} \left((\tfrac{9}{32} + \tfrac{3}{8}w + \tfrac{1}{4}w^2) \int_{-0}^{w/2} \cosh^{8/3} z \, dz - \int_0^{w/2} z^2 \cosh^{8/3} z \, dz \right)$$

$$I_3^{xc} = \xi_8^3\left(\frac{2}{\pi}\right)^{1/3}\frac{e^{-4w/3}}{w}\left((\tfrac{9}{8} + \tfrac{3}{2}w + w^2)\int_0^w \cosh^{1/3} z \, dz - \int_0^w z^2 \cosh^{1/3} z \, dz\right)$$

and

$$I_4^{xc} = \frac{\xi}{\pi^{1/3}}\frac{81}{64}\frac{e^{-4w/3}}{w}[\sinh(w/3)(4w/3 - 15) + \cosh(w/3)16w/3]. \tag{A7}$$

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